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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennysylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman......E. R. BRIDGWATER, E. I. du Pont de Nemours and Company
Vice-Chairman........ L. B. SEBRELL, Goodyear Tire and Rubber Company
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Sergeant-at-Arms..E. H. NAHM

General Spring Meeting of 1932—Detroit, Michigan

The meeting was held on February 25 and 26, 1932, in the Hotel Fort Shelby, with 135 members in attendance. The following program was given, with the exception of the paper by H. L. Wiley, which in his absence was read by title only.

C. E. Barnett. "The Reinforcement of Rubber by Pigments. The Effect of Size and Shape of Pigment Particles on the Stiffness of Rubber."

Howard L. Wiley. "Rubber Pigment Ratios in Batch Control."

John N. Street. "Grit in Carbon Black. The Effect on the Flexing Resistance of Vulcanized Rubber."

M. K. Easley and A. C. Eide. "The Effect of Cadmium Compounds on Typical Organic Accelerators during Vulcanization."

J. E. McCarty and Edward Cousins. "A Method for Maintaining Uniformity in Factory-Mixed Stocks."

E. W. Booth. "Heat-Resisting Inner Tube Stocks."

Donald W. Kitchin. "Studies in the Vulcanization of Rubber. V. Dielectric Constant and Power Factor of Vulcanized Rubber."

Harlan A. Depew. "Reaction between Zinc Soaps and Mercaptobenzothiazole."

F. H. Amon and R. K. Estelow. "Some Experiences with a Direct Accelerator Absorption Test."

T. C. Morris. "Solubility of Organic Compounds in Rubber."

N. A. Shepard and J. N. Street. "Effect of Curing Temperature on the Quality of Vulcanized Rubber."

R. K. Lee. "Automotive Rubber Problems."

T. Midgley, Jr., Albert L. Henne, and Mary Renoll. "Natural and Synthetic Rubber. IX. Constituents of the Rubber Hydrocarbon."

R. P. Dinsmore. Report of Physical Testing Committee.

H. L. Trumbull. Report of Papers Committee.

Business Meeting.

In the absence of the Chairman, H. L. Trumbull of the Papers Committee, the following report was given by H. L. Fisher:

"The Committee has been canvassed for an expression of opinion in regard to Chairman Bridgwater's suggestion that in addition to the two formal reviewers appointed to approve a paper for presentation and publication, papers be submitted to at least two other reviewers, who will be expected to lead a formal discussion at the meeting. The Committee is unanimous in approving this suggestion of Chair-

man Bridgwater, and suggests that the Rubber Division authorize all papers in the future to be submitted in quadruplicate, two copies of the paper to be sent out for formal review and approval and the other two copies for the review leading to the discussion. It is recommended by the Committee that this action be confirmed by the Rubber Division.

"One member of the Committee has suggested that in the future, when papers are sent to the various people for review, the name of the author of the paper be omitted so that the paper will be considered solely on its merits. He expresses the opinion that reviewers may be influenced to a certain extent by their personal opinion of the author, and that if the name of the author were withheld we might have a more unbiased and impartial review than those now obtained. At the time of this meeting not all the members of the Papers Committee have replied to letters which embodied this suggestion. It is, therefore, recommended that the matter be held in abeyance until the next meeting of the Rubber Division. Reports which are at present in the hands of the Chairman of the Papers Committee are in disagreement on this point.

"The members of the Division are asked to write to the Chairman of the Papers Committee if they have any opinions for or against this proposal. These opinions can then be given consideration by the Committee before the matter is drawn up for consideration at the Fall Meeting."

By vote of the Division the report was accepted.

In the absence of the Chairman, R. P. Dinsmore of the Physical Testing Committee, the following report was read by Warren H. Jones, and by vote of the Division accepted:

"The project before the Physical Testing Committee at the present time consists in carrying out a survey of the industry on the methods and equipment in use in the performance of oven-aging and oxygen-bomb tests on rubber samples. Fifty-nine questionnaires have been returned to the committee. These have been classified into six divisions as follows:

Mechanical Goods Manufacturers	14
Tire Manufacturers	13
Commercial Laboratories and suppliers	13
Insulated Wire Manufacturers	5
Rubberized Fabrics	9
Footwear	5

"The data from all these questionnaires have been classified, and were summarized at a meeting of the Committee held in Akron on February 19. The committee met again at the Detroit Meeting of the Division on February 25 and, after considering the summarized tabulations, agreed on tentative recommended practices for oven and oxygen-bomb aging. In the absence of the Chairman and several members, these tentative practices are being circulated to the committee members for final study. When this work is completed the committee will present the proposed methods to the Division for consideration. The committee therefore wishes to present this report on the progress of its activity."

H. E. Simmons, *Secretary-Treasurer*

Minutes of the Executive Committee Meeting—Hotel Fort Shelby, Friday, Feb. 26

E. R. Bridgwater, Chairman of the Division, called the meeting of the Executive Committee immediately following the adjournment of the Division. The following members were present:

E. R. Bridgwater, *Chairman*	N. A. Shepard
H. A. Winkelmann	L. B. Sebrell
S. M. Cadwell	H. E. Simmons, *Secretary-Treasurer*

After thoroughly discussing the question of a meeting place next Fall, it was voted unanimously by the Committee that the Fall Meeting be held with the American Chemical Society in Denver, Colorado.

By motion of the Executive Committee the Secretary was instructed to inform the Honorary members of the Rubber Division that in the future if they wished to receive RUBBER CHEMISTRY AND TECHNOLOGY it would be necessary for them to pay $4.00 per year.

The Committee authorized the authors to proceed and obtain advertising for RUBBER CHEMISTRY AND TECHNOLOGY as a means of aiding the publication of the Journal.

The Secretary's report was submitted and by vote accepted.

Total membership of the Division:		
Members	367	
Associate members	64	
Subscribers	64	
Honorary members	32	527
Members who have not paid for 1932	117	
Associate members not paid for 1932	51	168
Subscriptions not paid 24, mostly foreign.		
New members for 1932 (included in total membership)	19	
New subscribers for 1932	10	
Members and associates withdrawn due to unemployment or change of work	14	
Subscribers withdrawn	1	

H. E. SIMMONS, *Secretary*

The Treasurer's report was read and accepted.

Balance in the bank Sept. 1, 1931 (Buffalo Meeting)		$1270.92	
Amount received for dues and subscriptions		1688.97	
			$2959.89
Disbursements:			
Translations	$155.50		
Ben Franklin Printing Co.	55.94		
Mack Printing Co. (October issue)	1099.67		
Multigraphing	6.60		
Postage, telegrams, and office equipment	24.14		
Expenses of Secretary to Buffalo	45.00		
Refunds	4.00		
Stenographic services	60.00		
		$1450.85	

Collection of two English checks (one 25¢ and one 75¢)	1.00	
	——	1451.85
		$1508.04

H. E. Simmons, *Treasurer*

Group Meetings

Akron

March 7, 1932. Addresses on "The Oxides of Iron as Colors in Rubber," by J. W. Ayers (C. K. Williams & Co.), on "Zinc Oxides," by G. F. A. Stutz, George Haslam, and B. R. Silver (New Jersey Zinc Co.), and on "The Experiences of an Inventor," by A. J. Musselman. New officers: *Chairman,* H. F. Conroy (General Tire & Rubber Co.); *Vice-Chairman,* H. A. Bourne (Goodrich Co.); *Secretary-Treasurer,* E. H. Baker (Binney & Smith Co.). Attendance 200.

Boston

April 7, 1932. Addresses on "Some Effects of Heat in the Vulcanization of Rubber," by W. K. Lewis (Mass. Institute of Technology), and on "The Romance of News Gathering," by A. H. Blackington. New officers: *Chairman,* W. E. Glancy (Hood Rubber Co.); *Secretary-Treasurer,* J. J. Sindler (Converse Rubber Co.). Attendance 115.

Chicago

January 15, 1932. Addresses on "The Properties of Duprene," by E. R. Bridgwater (E. I. du Pont de Nemours & Co.), and on "Abrasion as a Measurement of Quality of a Rubber Compound," by H. A. Depew (New Jersey Zinc Co.).

March 18, 1932. Address on "The Sources of the Rubber Hydrocarbon," by N. van Cleef (Van Cleef Bros.).

Los Angeles

February 2, 1932. Address by F. H. Banbury on "The Banbury Mixer." New officers: *Chairman,* Philip Ritter; *Vice-Chairman,* R. E. Hutcheson; *Secretary,* W. R. Hucks. Attendance 58.

New York

December 16, 1932. Addresses on "Applications of Latex," by J. Edwardes (Heveatex Corp.), and on "The Influence of Applied Science on the Development of Industrial and Business Relations," by C. S. Ching (U. S. Rubber Co.). New officers: *Chairman,* John P. Coe; *Secretary-Treasurer,* Peter P. Pinto. Attendance 200.

New Books and Other Publications

Eighth Report on Native Rubber Cultivation. Third Quarter, 1931. Prepared by the Division of Agricultural Economics of the Information Service for Agriculture and Fisheries, Netherlands East Indian Department of Agriculture, Industry, and Commerce. Batavia, D.E.I. 14 pp. December, 1931.

The pamphlet is the latest of a series of reports dealing with the developments in native rubber production in the Dutch East Indies and carries the latest official statistics. It takes up in detail the production in various areas including Acheen, Tapanoeli, and the Riouw archipelago. [From *The Rubber Age* of New York.]

Rubber Producing Companies. Compiled by The Mincing Lane Tea & Rubber Share Brokers' Assn., Ltd., London, England. 1931. Published by *The Financial Times*, Ltd., 72 Coleman St., E. C. 2.

This standard work of rubber companies follows the lines of previous editions. The authentic and exhaustive information listed concerning over 600 companies includes capital, acreage, latest accounts, crops, purchase price, dividends, forward sales, estimates, etc. Directors and secretaries are listed. [From *India Rubber World.*]

Men Working: A Story of the Goodyear Tire & Rubber Company. By Norman Beasley. Published by Harper & Brothers, 49 East 33rd Street, New York City. 1931. 316 pp. $3.

A story that is familiar to rubber men has been interestingly recounted for the general public by a writer who has previously distinguished himself by similar industrial histories. Mr. Beasley presents a humanized biography of "men working" to build up from debts, patent litigations, and disappointments, a great industrial corporation, giving particular emphasis to the leadership of Paul Weeks Litchfield. It is, however, a selection of incidents rather than a complete portrayal of the company's growth. No mention is made of the tire price battles, of the 1926–1927 litigation that held national attention in the financial world, or of Goodyear's work in the World War. One-quarter of the Goodyear story is devoted to lighter-than-air development, although the catastrophes that attended the early experiments are omitted. The company's dealings with its employees comprise a large portion of the volume. Popular in style, with imaginary dialogue carrying the narrative along, the book at least makes interesting reading and should be informative for those not acquainted with the history of the rubber industry. [From *The Rubber Age* of New York.]

The World's Struggle with Rubber. By James Cooper Lawrence. Published by Harper & Bros., 49 East 33rd Street, New York City. 1931. 151 pp.

The author, Dean Lawrence, now of the faculty of Michigan University, is well equipped to write this review of rubber's part in the world's economic life, in view of his ten years' previous experience with the Goodrich company. Besides being a comprehensive history of the rubber producing industry it mainly stresses the inadequacy of American sources of supply and reviews the workings of the Restriction policy of Great Britain between 1922–1927. [From *The Rubber Age* of New York.]

The fortunes of the rubber industry have become, it would seem, a fashionable subject for treatises by professors at American Universities. It must be confessed that for the light which it throws on the future of rubber or on the possibility of world-planning and supply control generally, the book might as well never have been written. Although the author can claim practical experience in rubber manufacturing, he has not been preserved from the dogmatism associated with the

academic mind. At the same time, the corresponding academic virtue of objective approach to facts is unfortunately absent. Indeed, the book would appear to have been written more for expressing his feelings against the British than for the purpose of giving an unbiased and reliable history of the efforts to regulate the supplies of rubber during the last twenty years.... [From *Bulletin of the Rubber Growers' Association.*]

Rubber Roadways. Issued by Rubber Roadways, Ltd., London. 1931. 22 pp. For free distribution.

A review of the developments in rubber roadways from their first inception to date. Technical details have been avoided but the entire history of rubber roadway surfacing is adequately covered. The pamphlet is interestingly illustrated. [From *The Rubber Age* of New York.]

Rubber Latex. Circular Letter LC-321, Bureau of Standards, Washington, D. C. 35 pp. Free distribution. Feb. 25, 1932.

The pamphlet is intended to give general information on the subject of rubber latex and to direct interested parties to the sources from which special or detailed information may be obtained. Part I is a brief description of the production, composition, and properties of latex and its application in manufacturing processes. Part II is a bibliography on the subject of latex, covering publications over the period from 1927 to 1931, and is very complete and comprehensive. [From *The Rubber Age* of New York.]

L'Ebanite. By R. Ariano. Printed in Spanish. Reprinted from *Politecnico* No. 12, and published by Casa Editrice Dott, Francesco Vallardi, Milan, Italy. 1931. 16 pp.

The author reviews the history of ebonite and scientifically treats of its composition, mechanical qualities, resistancy to abrasion, and other properties. He also details the manufacturing processes. [From *The Rubber Age* of New York.]

Symposium on Rubber. American Society for Testing Materials, Phila., Pa. 116 pp. March, 1932. For free distribution.

The booklet includes the papers presented at the regional meeting of the Society, held at Cleveland, March 9, 1932. Abstracts of all the papers were printed in *The Rubber Age*, February 10, 1932. It is well illustrated with photographs and charts. [From *The Rubber Age* of New York.]

Control of Quality and Costs in Batch Mixing and Compounding of Rubber and Heavy Plastics. Bulletin No. 167. Published by Farrel-Birmingham Company, Ansonia, Conn. 6 pp. 1932. For free distribution.

Production data on the application of Banbury mixers in rubber compounding, with diagrams and detailed description of operation. [From *The Rubber Age* of New York.]

Bureau of Standards. Annual Report of the Director. Fiscal Year ending June 30, 1931. Government Printing Office, Washington. 50 pp. Price 15 cents.

The report summarizes the work of the Bureau of Standards during the past fiscal year. A number of subjects of interest to the rubber industry are outlined, notably the progress in the investigation of the chemical nature of rubber, the preparation of 46 standard federal specifications for rubber, and the testing of elastic cements. [From *The Rubber Age* of New York.]

A. S. T. M. Tentative Standards, 1931. Published by the American Society for Testing Materials, 1315 Spruce Street, Philadelphia, Pa. 1931. 1008 pp. $7 (paper); $8 (cloth).

The 1931 edition of A. S. T. M. Tentative Standards contains 180 tentative specifications, methods of test, definitions of terms, and recommended practices in effect at the time of publication, together with tentative revisions in 50 existing A. S. T. M. standards. Thirty of the tentative standards relate to rubber products, insulating materials, and textile materials. The volume contains a comprehensive subject index and a table of contents which lists, under the various materials covered, the respective standards. [From *The Rubber Age* of New York.]

"Proceedings of the Thirty-fourth Annual Meeting." This meeting was held at Chicago, Ill., June 22–26, 1931. Vol. 31, Parts I and II. American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Cloth. Illustrated, subject and author indices. Part I, 1119 pages; Part II, 1027 pages.

Part I contains the annual reports of the Society Committees, and the papers and standards appended. In this part of the 1931 proceedings are reports of 42 standing and research committees and reports of one joint and 2 sectional committees. Of special interest to the rubber industry are tentative specifications for rubber products, textile materials, and methods for the chemical analysis of rubber products.

Part II comprises the technical papers given at the annual meeting of the Society in June, 1931. The abrasion testing of rubber is a subject of interest to all producers and users of rubber and rubber products. A symposium on this subject is given in this volume. Comprising 60 pages it covers such subjects as tear resistance of rubber compounds, abrasion tests of these compounds, and a comparison of the tests made on several types of abrasion machines. [From *India Rubber World.*]

Cotton Cloth for Rubber and Pyroxylin Coating. Commercial Standard CS32-31. Published by the U. S. Bureau of Standards, Dept. of Commerce. Copies 5 cents. Government Printing Office, Washington, D. C. 1931. 14 pp.

The pamphlet details the specifications of the accepted standard for cotton cloth for rubber and pyroxylin coatings and covers the construction, quality, sizing, methods of test, and labeling of such products. The standard as adopted has had the endorsement of business firms and trade associations interested in this line of manufacture. [From *The Rubber Age* of New York.]

Principles of Patent Law for the Chemical and Metallurgical Industries. By Anthony William Deller. Published by the Chemical Company, 419 Fourth Avenue, New York City. 1931. 486 pp. $6.

The rubber industry, like many other fields of industrial activity, has felt the effect of the multiplicity of inventions in the realm of chemistry in recent years. All of the larger companies have been making their own researches, and the problem of patent protection has been frequently encountered. A volume of this type should be of great value in preventing costly mistakes as regards the protection of the results of such development work. Dr. Deller presents a great variety of information in an interesting way and offers as an appendix some statistics of foreign countries, data on foreign patents, and some valuable memoranda on minerals and metals. [From *The Rubber Age* of New York.]

Bibliography of Bibliographies on Chemistry and Chemical Technology. Bulletin of the National Research Council, No. 86. 150 pp. 1932. $1.50.

As the title indicates the work is a compilation of bibliographies, published as separates, or at the end of books or magazine articles, or as footnotes to the same, on the numerous aspects of pure and applied chemistry. Each entry gives the name of the author or compiler, and title and place of publication. The entries are conveniently classified under subject headings, alphabetically arranged. There are

numerous references pertaining to rubber chemistry and technology. [From *The Rubber Age* of New York.]

Kolloidchemische Technologie. A Handbook of the Colloid-Chemical Point of View in the Chemical Industry and Technology. Edited by Raph. Ed. Liesegang. Second completely revised edition. Paper or half-leather, in one volume or 13 parts; 1085 pages, 376 illustrations, 2 plates, numerous tables, $7^1/_2$ by $10^3/_8$ inches. Published by Theodor Steinkopff, Dresden and Leipzig, Germany, 1931.

Although the first edition of this work appeared in 1927, it became necessary to publish a second edition in the summer of 1931. The entire work has been thoroughly revised and brought up-to-date, and various new subjects, as "Plasticity and Plastification," have been included. The work is divided under 37 different heads, each contribution coming from an expert, and includes: "Active Carbons," by W. Mecklenburg; "Plasticity and Plastification," by J. Obrist; "Plastic Masses," by O. Manfred; "Rubber," by E. A. Hauser; "Electrotechnical Insulating Materials," by H. Stager; and "Electroösmosis," by E. Mayer. There is also a concluding chapter by Liesegang, which is in the nature of a guide to the use of the book and an exposition of his introductory remarks:

"The reader will notice how the application of a certain colloid-chemical conception is still in its infancy in one field; whereas in another it was in use long before a formal colloid-chemistry existed. There is an immediate inducement to learn from the latter in favor of that which has been treated in such step-motherly fashion. This is often possible, however unrelated two fields may appear to be."

The work is supplied with an index of authors and an alphabetical index of subjects, besides a detailed table of contents. [From *India Rubber World.*]

Notice to Readers

The abstracts of articles from academic, engineering, industrial, and trade journals, which have heretofore been published in conjunction with the patents in RUBBER CHEMISTRY AND TECHNOLOGY, have been discontinued. These abstracts have not been indexed, and therefore are of little permanent value. To certain of our readers, to whom *Chemical Abstracts* itself is not available, they may of course have a temporary value. In view of the relatively small interest in this feature, it is felt that the expenditure necessary for the abstracts is too great to warrant their publication in the future.

The patents are continued in this issue, but with the intention of discontinuing them likewise unless there is a wide enough appeal to justify their continuation. The Editors therefore encourage any subscribers to send their opinions on this subject, but unless a sufficient number respond in favor of the inclusion of patents, the latter will be discontinued hereafter.

THE EDITORS

A Survey of Recent Chemical Patents on Rubber

Abstracts of Patents Which Have Been Issued in the United States and Elsewhere

The following abstracts of patents are reprinted from the January 10, and 20, February 10 and 20, March 10 and 20, and April 10 and 20, 1932, issues of *Chemical Abstracts*.

Acrolein condensation products. WALTER KROPP (to I. G. Farbenind. A.-G.). U. S. 1,845,755, Feb. 16. Compds. which may be used as rubber-vulcanization accelerators are formed by causing an α,β-dialkyl-substituted acrolein such as α-ethyl-β-propylacrolein or α-isopropyl-β-isobutylacrolein to react with a primary aromatic amine such as aniline (suitably in the presence of an inert solvent such as C_6H_6 and a condensing agent such as $ZnCl_2$). Cf. *C. A.* **26**, 1157.

Films, threads, disks, etc. I. G. FARBENIND. A.-G. Fr. 39,424, Nov. 26, 1930. Addn. to 676,658 (*C. A.* **24**, 3135). The sulfuring process of Fr. 676,658 is applied to products made from natural rubber. The products of Fr. 676,658 and of this patent are improved by incorporating therewith paraffinic hydrocarbons of high mol wt., cycloparaffins or natural or artificial waxes.

Treating rubber to retard vulcanization or cracking. SYDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,844,943, Feb. 16. A rubber stock is treated with ethyl oxalate, butyl citrate or other suitable ester of an acid having a dissocn. const. equal at least to 6.6×10^{-5} at 25°. Cf. *C. A.* **26**, 1830.

Retarding the cracking of rubber masses. THE NAUGATUCK CHEMICAL CO. Ger. 538,942, Nov. 3, 1929. The cracking of rubber is retarded by treatment with compds. contg. the group $\equiv$CCOCOC$\equiv$ before or during vulcanization. Examples of such compds. are α-diketones such as benzil, furil and phenanthrenequinone.

Apparatus for vulcanizing rubber tires. OTTO J. KUHLKE (to National Rubber Machinery Co.). U. S. 1,844,962, Feb. 16. Mech. features.

Age-resisting vulcanized rubber. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,845,346, Feb. 16. Vulcanization is effected in the presence of an antioxidant (suitably about 5% or less) formed by neutralizing the soln. obtained by digesting (at about 35–50°) the reaction product of equimol. proportions of a hydroxy aliphatic aldehyde and a primary aromatic amine such as acetaldol and aniline with substantially an equiv. proportion of a strong inorg. acid such as HCl. U. S. 1,845,347 relates to a process in which vulcanization, with use of S and an accelerator,

is effected in the presence of a non-polymerized ring-substituted quinoline with less than 3 substituent groups, such as dimethylquinoline, naphthoquinoline or 2-phenylquinoline. Cf. *C. A.* **26**, 1158, 2085.

Vulcanizing rubber. Robert H. M. L. Binay and Louis F. Pecot. Fr. 39,143, Oct. 2, 1930. Addn. to 682,521 (*C. A.* **24**, 4666). The compn. described in Fr. 682,521 is covered with a layer of gum lac or other protecting substance after it is placed in the mold.

Vulcanizing rubber. E. I. du Pont de Nemours & Co. Ger. 540,944, Mar. 6, 1926. Crude rubber is vulcanized with the employment of accelerators formed by the direct condensation of 1 mol. of a primary amine with 2 or more mols. of a satd. aldehyde in an acid medium. Examples mention products from heptaldehyde and butylamine, aniline and butyraldehyde and butyraldehyde and butylamine.

Vulcanizing natural or synthetic rubber. Metallgesellschaft A.-G. (Paul Scholz, inventor). Ger. 540,631, June 3, 1927. The vulcanizing process is accelerated and the product rendered more tough by adding a small quantity of Se in the form of a condensation product from NH_3, H_2Se and an aldehyde. Examples are given.

Rubber. The Anode Rubber Co., Ltd. Ger. 530,669, May 28, 1927. Cohesive coagulated coatings are formed on pptd. underlayers by aq. dispersions of rubber-like material mixed with a suitable amt. of hydrophile gel-forming material. Examples are given.

Preserving latex. Alexander A. Nikitin (to Naugatuck Chemical Co.). U. S. 1,823,119, Sept. 15. A stable uncoagulated rubber latex is prepd. contg. saponin, arbutin or salicin and having a p_H not higher than 7. Cf. *C. A.* **25**, 3521.

Preserving rubber. Albert M. Clifford (to Goodyear Tire & Rubber Co.). U. S. 1,823,531, Sept. 15. Rubber is preserved by addn. (suitably of about 1%) of a reaction product of a naphthol with ethylenediamine or phenylenediamine.

Rubber compositions. Compagnie Lorraine de charbons pour l'electricité. Ger. 532,094, Dec. 1, 1927. A filler for rubber is prepd. by mechanically mixing soot with about 10% of tar without the aid of a solvent.

Rubber deposition. The Anode Rubber Co. (England), Ltd. Fr. 37,993, Feb. 4, 1930. Addn. to 657,948. The conversion of the neg. charge of the particles to a pos. charge is carried out in the presence of protective colloids such as casein, hemoglobin or saponin.

Highly viscous aqueous dispersions of rubber, gutta-percha, or balata. Max Forrer (to Anode Rubber Co. Ltd.). U. S. 1,825,515, Sept. 29. An aq. soln. of a completely hydrolyzed gel-forming protein substance such as gelatin in hot aq. soln. is added to a dispersion of rubber or the like to increase the viscosity of the dispersion above that which would be obtained by concn. alone before the point of inversion of the dispersion is reached.

Reducing the tacky character of rubber surfaces. Paul A. Davis (to Goodyear Tire & Rubber Co.). U. S. 1,823,855, Sept. 15. Surfaces of uncured rubber are dusted with an Al or Mg soap.

Sponge rubber. Paul H. Richert. U. S. 1,823,335, Sept. 15. A ground NH_4 bisulfite is introduced into the rubber during plasticizing and it is subsequently heated sufficiently to decompose the bisulfite and effect vulcanization.

Rubber sponge. Yves Cornic. Ger. 532,457, June 29, 1929. See Brit. 314,539 (*C. A.* **24**, 1545).

Decorating rubber. Bert S. Taylor (to B. F. Goodrich Co.). U. S. 1,825,252, Sept. 29. Soft rubber articles such as balloons, bath caps, etc., comprise a vulcanized, colored, extensible rubber base, a single layer of finely divided flaked metal such as Al or Cu uniformly distributed over at least a portion of the base, and a transparent extensible coating such as a rubber cement over the metal layer.

Coloring rubber, etc. Hans Tochtermann (to I. G. Farbenind. A.-G.). U. S. 1,823,921, Sept. 22. There is incorporated with the material, before vulcanization, a coloring matter in the form of an aq. paste contg. a difficultly volatile org. substance, *e. g.*, a paste contg. "Brilliant indigo 4 G" or Sb sulfide and an alc. b. above 100°. Various examples are given. Cf. *C. A.* **25**, 2876.

Coloring synthetic rubber. I. G. Farbenind A.-G. Brit. 345,239, Dec. 16, 1929. In a process generally similar to the process described in Brit. 241,214 (*C. A.* **20**, 2596), coloring components are incorporated with dissolved or emulsified intermediate products such as butadiene or isoprene used for the manuf. of synthetic rubber, the components are converted into insol. coloring substances and solid synthetic rubber is then produced from the colored material. Numerous details and examples are given.

Pigments for rubber. Compagnie française de l'iode et de l'algine. Fr. 706,529, Mar. 3, 1930. A pigment intensifier for rubber mixts. is made from algine

and its derivs. by submitting algine or alginic acid extd. from marine algae or Al alginate to formolization before making it into an aq. paste. The formolization may be carried out in the presence of NH_3.

Forming rubber articles by dipping. THE ANODE RUBBER CO., LTD. Ger. 532,347, May 6, 1927. See Brit. 287,946 (*C. A.* **23,** 547).

Coating metals with rubber. ALEXANDER JENNY. Ger. 532,346, Dec. 13, 1927. See Brit. 302,250 (*C. A.* **23,** 4375).

Rubber on aluminum. SOC. ANON. DES ATELIERS D'AVIATION LOUIS BREGUET. Fr. 706,480, Feb. 25, 1930. Rubber is made to adhere to Al or its alloys by first electrolytically depositing a thin layer of Fe on the metal to be covered and then molding the rubber thereon in the usual manner.

Synthetic rubber. ERNST KLEIBER and PIERO GILARDI. Swiss 146,279, Sept. 2, 1929. An elastic mass capable of vulcanization is obtained by direct polymerization of mineral oil by agitation with H_2SO_4, a small quantity of caoutchouc being present during the process to act as a priming.

Rubber substitutes. I. G. FARBENIND. A.-G. (Walter Bock and Eduard Tschunkur, inventors.) Ger. 532,271, Jan. 16, 1930. Aq. emulsions of butadiene hydrocarbons, with or without olefins of the C_6H_6 series, are polymerized in the presence of chlorinated org. compds., *e. g.*, C_2Cl_6, $C_2H_2Cl_2$, or CCl_4. Examples are given. Cf. *C. A.* **25,** 4443 and following abstracts.

Rubber substitutes. I. G. FARBENIND. A.-G. (Georg Ebert, Friedrich A. Fries and Paul Garbsch, inventors). Ger. 532,455, June 11, 1929. Diolefins are polymerized by treatment with alkali or alk. earth metals, or their alloys or mixts., in the presence of org. compds. in which at least 2 valencies of the same C atom are linked to O, *e. g.*, a cyclic acetal such as that from crotonaldehyde and butylene glycol. Examples are given.

Rubber substitutes. I. G. FARBENIND. A.-G. (Eduard Tschunkur and Walter Bock, inventors). Ger. 532,456, July 21, 1929. Mixed polymerization products of butadienes and of olefins of the C_6H_6 series, or their substitution products, are vulcanized after incorporation of soot. Examples are given.

Rubber substitute. MARTIN BANDLI. Fr. 706,319, Nov. 24, 1930. A rubber substitute is made by dissolving nitrocellulose in a mixt. of solvents in which one or more plastifying agents are dissolved or suspended, after which the nitrocellulose and plastifying agent are pptd. by an appropriate liquid. Of the solvents one at least is easily miscible with the pptg. liquid and one at least is more difficultly miscible. In examples, a mixt. of acetone, ether and MeOH or EtOH is used as solvents, tricresylphosphate as plastifying agent and water as pptg. agent.

4,4'-Diaminodiphenylmethane. C. COLEMAN (to Naugatuck Chemical Co.). Brit. 344,174, Feb. 15, 1929. This compd. is prepd. by treating aniline with formaldehyde at 40° for 2 hrs., sepg. water, and adding aniline-HCl or HCl and heating at 80° for 24 hrs., neutralizing the acid and distg. off water and aniline. The product, and its condensation product with 0.5 or 1 mol. proportion of formaldehyde, may be used to *retard aging of rubber*.

Rubber vulcanization accelerators. WILHELM LOMMEL, THEODOR GOOST and HERMANN FRIEDRICH (to I. G. Farbenind. A.-G.). U. S. 1,824,609, Sept. 22. As accelerators, there are used compds. such as decahydroquinaldine, the Zn salt of cyclohexylethyldithiocarbamic acid, the cyclohexylethylamine salt of cyclohexylethyldithiocarbamic acid, the thiuram disulfide of decahydroquinaldine, the thiuram monosulfide of cyclohexylethylamine and other compds. of like character and structure.

Piperidine salt of pentamethylenedithiocarbamic acid. GEORGE LUTZ (to E. I. du Pont de Nemours & Co.). U. S. 1,823,499, Sept. 15. Piperidine and CS_2 are brought into contact in a solvent such as gasoline which is inert to the reacting materials, is liquid at ordinary temp. and b. below about 250°. The product seps. as colorless crystals and may be used as a *rubber vulcanization accelerator*.

Thiuram polysulfides. ROESSLER & HASSLACHER CHEMICAL CO. Ger. 530,822, Jan. 21, 1927. See *C. A.* **22,** 4008 (U. S. 1,681,717).

Apparatus for vulcanizing rubber-covered wire. WILLIS J. PEELLE. U. S. 1,825,282, Sept. 29. Structural and mech. features.

Rubber vulcanization. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,825,288, Sept. 29. Rubber and S are heated in the presence of an accelerator which is the reaction product of an aldehyde deriv. of a Schiff's base and the product formed by the reaction of a mercaptobenzothiazole and $(CH_2)_6N_4$. Cf. *C. A.* **25,** 438.

Concentrating latex. K. D. P., LTD. Ger. 533,373, July 16, 1927. Latex that has been protected against coagulation by addn. of alkali is neutralized or rendered acid by addn. of a soap-forming fatty acid, and then concd. Cf. *C. A.* **25,** 4740.

Thickening latex. VEEDIP, LTD. Ger. 533,068, Mar. 25, 1928. See Brit. 312,947 (*C. A.* **24**, 988).

Thickening and stabilizing latex. MERWYN C. TEAGUE (to American Rubber Co.). U. S. 1,826,192, Oct. 6. The continuous phase is thickened and the latex stabilized without substantial modification of the colloidal condition of the rubber hydrocarbon by adding any of the following substances: Pb thiosulfate, basic Pb acetate, lead acetate with a protective agent, PbO, Pb hydroxide, the reaction products of Pb oxides or salts with mono-, di- and poly-saccharoses, Pb chloride, Bi hydrate, Fe_2O_3, ferrous lactate, basic ferric acetate, ferrous oxalate, stannous oxalate, CdS.

Composition comprising animal fibers and latex. ANTONIO FERRETTI (to Società invenzioni brevetti anonima-Torino). U. S. 1,827,356, Oct. 13. A vulcanizing agent such as colloidal S is added to a slurry of animal fibers such as hide scraps and a latex binder in aq. suspension, and before vulcanization has proceeded to a detrimental degree liquids are extd. from the slurry. The product may be used for making vulcanized sheets.

Rubber goods from latex. ROBERT A. DUNHAM (to Union Oil Co. of Calif.). U. S. 1,826,392, Oct. 6. A latex contg. a sludge oil or Edeleanu ext. is used for making rubber articles on dipped forms or by other methods.

Rubber goods produced directly from latex. PAUL KLEIN and ANDREW SZEGVARI (to American Anode, Inc.). U. S. 1,825,736, Oct. 6. In producing rubber goods directly from aq. rubber dispersions, there is assocd. with a mold a substance such as $CaCl_2$ or $ZnCl_2$ which is capable of agglomerating rubber particles in the dispersion, and the mold is immersed in the aq. dispersion for such a time as to permit some of the agglomerating substance to diffuse into the dispersion to form about the mold a coherent layer of deposited rubber. U. S. 1,825,737 (PAUL KLEIN—to Am. Anode, Inc.) describes a process involving the removal of water from rubber deposits produced from aq. dispersions, by permitting at one side of the deposited layer a free escape of moisture and maintaining a higher temp. at the other side of the deposit. U. S. 1,825,738 (PAUL KLEIN and FRANCIS GABOR—to Am. Anode, Inc.) describes a process of rubber deposition from aq. dispersions by repeated dipping, in which the dipping mold is heated during the intervals between the dippings (and if desired also during the dipping, as by an elec. current).

Treating rubber. THE NAUGATUCK CHEMICAL CO. Fr. 706,986, Dec. 3, 1930. Rubber and like materials are treated with the reaction product of a ketone and an aromatic amine or amino compd., or with the naphthol addn. products of the same, or with the aldehyde derivs. of the same. The above compds. retard the deterioration of rubber, improve its resistance to abrasion, prevent cracking of tread stocks contg. carbon black and improve the resistance of vulcanized rubber to tearing. A long list of compds. which may be used is given, including acetone-aniline, acetone-phenylhydrazine, acetone-diphenylformamidine, acetone-diphenylguanidine, the β-naphthol addn. compd. of acetone-aniline, the reaction product of CH_2O and acetone-aniline and the reaction product of CH_2O and chloroacetone-aniline. Several examples are given. Fr. 706,987 describes the use for the same purpose of the reaction product of a ketone and an aldehyde-aromatic amine condensation product, the reaction product of a ketone and a salt of an aromatic amino compd., a rearranged reaction product of a ketone and an aromatic amino compd., a rearranged reaction product of a ketone and an aromatic amino compd., or the naphthol addn. product or aldehyde derivs. of the foregoing, or a naphthol reaction product of a rearranged reaction product of a ketone and an aromatic amino compd. (in this case water is split off). A long list of suitable compds., and several examples are given. Cf. *C. A.* **25**, 6017–8.

Mixing machine for agitating or masticating rubber compositions. DUNLOP RUBBER CO., LTD., and P. D. PATTERSON. Brit. 346,446, Jan. 13, 1930. Mech. features.

Mixing machine for rubber and plastic masses. CARL F. SCHNUCK and FERNLEY H. BANBURY. Ger. 532,718, Sept. 18, 1930.

Rubber depositions. THE ANODE RUBBER CO., LTD. Fr. 706,876, Sept. 16, 1930. Rubber and like plastic substances are deposited electrolytically in a layer of uniform thickness from an aq. emulsion under such conditions that the resistance of the deposit formed increases more rapidly than its thickness. The regulation of the variation of the elec. resistance of the deposit as a function of its thickness is effected by acting on the alky. and the resistivity of the aq. emulsion. Cf. *C. A.* **26**, 336.

Porous rubber. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 706,999, Dec. 3, 1930. Articles of porous or microporous vulcanized rubber are made from aq. emulsions or dispersions of rubber, gutta-percha, etc., by operations such

as electrophoresis, dipping, spreading, impregnating, spraying or molding. The admixt., in the operation used, of electrolytes which tend to produce gelling of the aq. emulsions or dispersions in the cold or with heat is excluded. The articles are then vulcanized under such conditions that evapn. of the liquid contained in the pores or micropores is avoided.

Retarding oxidation of organic materials such as rubber compositions. LUDWIG J. CHRISTMANN (to American Cyanamid Co.). U. S. 1,825,654, Oct. 6. Tribenzylamine (suitably about 1%) is added as an oxidation retarder, and for the same purpose there may also be used similar compds. such as methyldiphenylamine, methylbenzylaniline, etc.

Chlorinated rubber product. FRANCIS C. DYCHE-TEAGUE. U. S. 1,826,275, Oct. 6. Rubber is oxidized (suitably by air or O at 60° or above), the oxidized product is "disaggregated" by rolling in a mill, a soln. is formed from the material after this treatment, and Cl is passed through the soln. The product is suitable for manuf. of molded articles or use in coating compns. Cf. *C. A.* **25,** 5797.

Forming rubber goods by precipitating the rubber from an aqueous dispersion, on a porous form. MORGAN & WRIGHT. Ger. 532,813, Feb. 1, 1929.

Rubber articles. ERNST A. HAUSER. Ger. 533,066, Sept. 11, 1926. For the manuf. of rubber articles of complex shape, moist latex of creamy consistency is sprayed on to a mold. The latex may contain vulcanizing agents, fillers and pigments. An example is given.

Artificial rubber. EDUARD TSCHUNKUR and WALTER BOCK. U. S. 1,826,846, Oct. 13. Vulcanizates are produced by vulcanizing a mixt. of at least 2 different polymerization products of diolefins such as butadiene, isoprene and dimethylbutadienes in the presence of about 30–80% its wt. of finely divided carbon black. Such vulcanizates have indices of strength between about 50,000 and 190,000.

Emulsifying agents for preparing artificial rubber. I. G. FARBENIND. A.-G. Brit. 346,387, Jan. 2, 1929. α-Diethylamino-β-hydroxypropylamine is condensed with oleic acid, ethyl oleate or stearic acid and α-diethylamino-β-hydroxy-α-phenylaminopropane is condensed with oleic acid chloride or stearic acid chloride, or similar condensations are effected to prepare emulsifying agents.

Vulcanization accelerators. DUNLOP RUBBER CO., LTD. Fr. 707,052, Dec. 4, 1930. Vulcanization accelerators for rubber are produced by replacing an atom of H of the thiol group in mercaptobenzothiazole and like products by a neg. org. radical or acyl group, *e. g.*, a benzoyl, nitrobenzoyl, stearyl or palmityl group. Examples are given of the prepn. and use of these compds.

Low-temperature vulcanization of rubber with stable chemically active selenium sulfide. BIRGER W. NORDLANDER (to General Elec. Co.). U. S. 1,827,604, Oct. 13.

Cold-vulcanizing rubber. ARTHUR EICHENGRÜN. Ger. 533,288, Mar. 21, 1925. Use is made of a soln. of S_2Cl_2 or its equivalent in CH_2Cl_2, with or without CS_2 or other rubber solvent. Exptl. results are given.

Reclaiming waste vulcanized rubber. WM. B. PRATT (to Dispersions Process, Inc.). U. S. 1,826,091, Oct. 6. The material is first agitated in the presence of moisture to effect absorption of moisture and swelling of the rubber particles, and the moistened stock is then kneaded in the presence of a softener such as rosin oil, pine tar or petrolatum until a plastic mass is formed. Cf. *C. A.* **25,** 4444.

Purifying and separating rubber latex. HANS O. LINDGREN (to DeLaval Separator Co.). U. S. 1,831,500, Nov. 10. Various details of app. and operation are described for effecting centrifugal sepn. to obtain a purified latex of relatively high-rubber content and a purified latex of relatively low-rubber content.

Concentrating latex. ERNST A. HAUSER. U. S. 1,831,492, Nov. 10. In concentrating latex by adding mucilages or substances which combine with water, the rubber dispersions treated are heated to above 90° in order to facilitate complete sepn.

Latex composition. WALLACE B. VAN ARSDEL and ROGER B. HILL (to Brown Co.). U. S. 1,831,895, Nov. 17. A compn. suitable for coating or impregnating fibrous sheet materials comprises a purified, concd. mixt. of vulcanized latex and more than 25% unvulcanized latex, resulting from creaming and sepg. from a substantial portion of the water component of the unconcd. mixt. and non-rubber solids present in the aq. component.

Rubber. WM. FELDENHEIMER and WALTER W. PLOWMAN. Ger. 533,633, Mar. 16, 1924. See Brit. 218,364 (*C. A.* **19,** 909).

Rubber hydrocarbons. I. G. FARBENIND. A.-G. Fr. 707,458, Dec. 12, 1930. The pure hydrocarbons of rubber are obtained from rubber latex by treating the latex with an alkali lye in the presence of emulsifying agents sol. in water. An example is given of the use of Na oleate.

Electrophoretic separation of rubber. SIEMENS-ÉLEKTRO-OSMOSE G. M. B. H. Fr. 707,600, Dec. 16, 1930. Rubber is deposited by use of short-circuited electrodes of different materials and a depolarizing medium. The cond. of the dispersion is maintained below 600 × 10^{-4} ohms^{-1} cm^{-1}. The cathodes consist entirely or superficially of easily reducible metal peroxides. Sepn. of rubber is effected on the anode or on a porous mold in front of it. Detailed examples are given.

Rubber articles formed by deposition. PARKE H. WATKINS and ALBERT W. HOLMBERG (to National India Rubber Co.). U. S. 1,828,990, Oct. 27. In forming overshoes or other articles, a deposit of rubber compn. is continuously built up on a porous form by maintaining the form in contact with a body of aq. rubber dispersion and withdrawing the dispersing agent through the form, localized portions of the deposit being then alternately contacted with a rubber dispersion and with coagulant, followed by addnl. contact with rubber dispersion, drying and vulcanizing.

Spongy products from rubber dispersions. GEOFFREY W. TROBRIDGE, EDWARD A. MURPHY, DOUGLAS F. TWISS and WALTER G. GORHAM (to Dunlop Rubber Co., Ltd.). U. S. 1,828,481, Oct. 20. A froth of a dispersion of rubber material is molded to desired dimensions, the molded mass is heated from the exterior, and heat is conveyed into the interior of the mass in closely spaced parallel paths, as by heating tubes within the mold. App. is described.

Retarding aging of rubber compositions. WM. S. CALCOTT and WM. A. DOUGLASS (to E. I. du Pont de Nemours & Co.). U. S. 1,830,749, Nov. 10. A monohydroxy anti-oxidant such as *p*-hydroxybiphenyl or other suitable compd. of the general formula HO—R—R′, in which R and R′ represent aryl radicals, is added (suitably in the proportion of about 1%).

Extruding machine for forming rubber products such as tubing or threads. WILLIS A GIBBONS and EARDLEY HAZELL (to General Rubber Co.). U. S. 1,832,012, Nov. 17. structural features.

Finishing rubber articles. SEAPHES D. SHINKLE (to L. Candee & Co.). U. S. 1,828,985, Oct. 27. A rubber article such as footwear is coated with a varnish comprising an oxidizable oil such as linseed oil and S, followed by heat curing and superficial treatment with a medium contg. a low concn. of a halogen-supplying agent such as S chloride (and subsequent NH_3 treatment) in order to render the surface glossy and non-tacky. App. is described.

Rubber diaphragm for electrolytic cells, filters, etc. HERMANN BECKMANN. U. S. 1,831,406, Nov. 10. A porous rubber product is produced from a vulcanized latex coagulum, traversed by an "infinite number" of extremely fine pores of colloidal size invisible to the naked eye and filled with liquid such as a wood ext. or phenol capable of exerting a favorable effect on the neg. electrodes of Pb storage batteries.

Preventing water-bag deterioration in pneumatic tire manufacture. ERNEST T. HANDLEY (to Firestone Tire & Rubber Co.). U. S. 1,830,465, Nov. 3. A water bag is placed inside the green tire casing, the casing and bag are placed in a heated mold and water contg. Na sulfite as a deoxidizing agent is circulated through the bag under heat and pressure.

Synthetic rubber. I. G. FARBENIND. A.-G. (Arthur Beck and Martin Luther, inventors). Ger. 533,885, Oct. 18, 1927. Rubber-like polymerization products are obtained by stirring or shaking butadiene hydrocarbons with aq. liquids contg. polymerization promotors so that a creamy or jelly-like mass contg. at least 75% butadiene hydrocarbons results. An example is given.

Synthetic rubber. I. G. FARBENIND. A.-G. (Martin Luther and Claus Heuck, inventors). Ger. 533,886, Apr. 25, 1929. Rubber-like products are formed by polymerizing butadiene hydrocarbons by the aid of alkali metals or their alloys, or alkali org. compds. The hydrocarbons are polymerized in stages. Thus butadiene is treated with Na amalgam at 0–6° for 2 days. The temp. is then raised to 30–40°, Na added and the mass allowed to stand for several more days.

Rubber-like product. WM. S. CALCOTT, FREDERICK B. DOWNING and DONALD H. POWERS (to E. I. du Pont de Nemours & Co.). U. S. 1,829,502, Oct. 27. C_2H_2 is polymerized to a rubber-like product and an emulsion of the polymerized product (divinylacetylene) is coagulated. Numerous details of procedure are given.

Rubber substitute. I. G. FARBENIND. A.-G (Martin Luther and Hans Beller, inventors). Ger. 533,800, July 4, 1928. Linoxyn or factice-like products are produced by splitting off water from the oxidation products of paraffins, waxes, fatty acids or their esters with polyhydric alcs., by distn. or heating. Examples are given. Cf. *C. A.* **26,** 337.

Rubber-vulcanization accelerator. GEORGE S. WHITBY (to Roessler & Hasslacher

Chemical Co.). U. S. 1,832,163, Nov. 17. "Carbisopropoxy thione disulfide (Me_2-$CHOC(:S)S-)_2$, is used as an accelerator.

Apparatus for vulcanizing rubber footwear. James W. Schade (to B. F. Goodrich Co.). U.S. 1,829,018, Oct. 27. Structural and mech. features.

Vulcanizing rubber. George H. Stevens. U. S. 1,831,932, Nov. 17. Monophenylguanidine is used as an accelerator.

Rubber vulcanization. Winfield Scott (to Rubber Service Laboratories Co.). U. S. 1,832,328, Nov. 17. An accelerator is used which is prepd. by the reaction of a dithiocarbamate such as that of piperidine pentamethylene with a nitro-substituted phenylhalomercaptan such as *o*-nitrophenylchloromercaptan. Cf. *C. A.* **26**, 338.

Vulcanized rubber. I. G. Farbenind. A.-G. Fr. 707,206, Dec. 6, 1930. Vulcanized products of rubber or polymerization products of butadiene hydrocarbons are made by incorporating in the mixt. to be vulcanized ZnO obtained as a secondary product and purified by levigation. The ZnO may be that obtained as a secondary product in the prepn. of hyposulfite, CH_2O-sulfoxylates, of benzidine, etc.

Treating rubber latex. Willis A. Gibbons (to Naugatuck Chemical Co.). U. S. 1,834,148, Dec. 1. Sufficient NH_4 phosphate, NH_4 oxalate or NH_4 citrate is added to latex to give the water ext. of the dried latex a p_H of 6 or less, and rubber is manufd. from the latex by the evapn. method. Cf. *C. A.* **25**, 4149.

Treating rubber latex. Roger B. Hill (to Brown Co.). U. S. 1,837,162, Dec. 15. An uncoagulated latex is prepd. contg. added alkali such as NaOH and lime and also contg. colloids pptd. *in situ* in the latex in the form of Ca compds., including Ca compds. of colloids natural to the latex and Ca soap. The material thus treated is suitable for impregnating fibrous materials.

Latex treatment. Roger B. Hill (to Brown Co.). U. S. 1,836,595, Dec. 15. An uncoagulated latex is prepd. contg. the water-insol. Ca soap resulting from the reaction *in situ* in the latex of about 1% of sol. soap (calcd. on the wt. of the latex) and about 10% of CaO (similarly calcd.). This Ca soap serves to facilitate setting or coagulation.

Conditioning latex. Frederick W. Vogel, Paul Brown and Roger B. Hill (to Brown Co.). U. S. 1,834,481, Dec. 1. A 2–10% soln. of an acid reagent such as H_2SO_4 or HOAc is added, slowly and with stirring, to an alkali-preserved latex until the latex has a p_H of about 8.5–9.5. The material thus prepd. is *suitable for treating fabrics*, etc.

Conditioning latex. Roger B. Hill (to Brown Co.). U. S. 1,834,490, Dec. 1. An unvulcanized, substantially unthickened, NH_3-preserved latex is prepd. free from certain natural constituents by pptn. with ZnO and removal of the ppt.

Apparatus for manufacture of rubber articles such as inner tubes for tires from latex. Alexis W. Keen (to Morgan and Wright). U. S. 1,833,024, Nov. 24. Structural features.

Rubber. Franz Clouth Rheinische Gummiwarenfabrik A.-G. Ger. 537,031, June 24, 1930. Small particles of vulcanized soft rubber are obtained by disintegrating waste from the manuf. of rubber filaments on grinding rolls, the waste being wetted with a soap soln. before or during grinding.

Rubber. Technische Chemikalien-Co. G. m. b. H. Ger. 536,120, July 15, 1927. As softeners and anti-agers in the manuf. of rubber articles, use is made of oils obtained from coal tar, brown-coal tar or shale tar or their distillates by extn. withNaOH soln. and acidification of the ext.

Rubber. I. G. Farbenind. A.-G. (Erwin Walz, inventor). Ger. 535,687, Mar. 12, 1929. Transformation products of rubber are produced by treating the latter with phosphorus oxyhalides or mixts. of these with phosphorus halide. Thus, rubber is treated with $POCl_3$ and PCl_3. The rubber is isomerized giving a red-brown soln This is treated with gaseous NH_3 till a yellow soln. is produced which is dried *in vacuo*, washed with warm water and rolled to give a non-sticky product with the properties of balata.

Rubber. Deutsche Hydrierwerke A.-G. (Ernst Helft, inventor). Fr. 708,-501, Dec. 16, 1930. A better distribution of substances to be added to rubber, such as dyes or accelerators, is obtained by first forming the substance to be added into a paste with fatty alcs. of high mol. wt.

Rubber, etc. I. G. Farbenind. A.-G. Fr. 709,068, Jan. 9, 1931. The products obtained by treating bitumens, alone, in soln. or mixed with other substances of high mol. wt., with SO_2 or substances contg. it, are used as addns. to natural or synthetic rubber, gutta-percha, etc. The treatment with SO_2 may be combined with a treatment with H_2S. The SO_2 may be eliminated by heating while passing N or CO_2 through the mass. Examples are given.

Rubber composition. Frank O. Woodruff (to Harry H. Beckwith). U. S. 1,835,365, Dec. 8. Latex is mixed with an approx. equal wt. of a diluent such as a drying oil or an essential oil (or both), and there is stirred into the mixt. about 2% its wt.

of a 40% soln. of formaldehyde. The compn. thus prepd. is suitable for shipment without deterioration in transit.

Rubber compositions. I. G. FARBENIND. A.-G. (Eduard Tschunkur and Walter Bock, inventors). Ger. 537,035, June 18, 1929. Mixts. contg. both natural and synthetic rubber are vulcanized in the presence of soot. Various methods of prepg. the mixts. are indicated Examples are given.

Rubber compositions. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 709,712, Jan. 20, 1931. Rubber compns. are made by mixing fragments of spongy rubber, vulcanized rubber, paper pulp, asbestos, etc., which have been or are ultimately brought into the state of foam, and then transforming the foamy mixt. into an irreversible solid substance of spongy or cellular state.

Porous rubber. HERMANN BECKMANN. Fr. 38,424, April 28, 1930. Addn. to 606,989. Rubber with a large no. of microscopical pores is prepd. by transforming the rubber latex into a pulp by the addn. of salts having univalent cations and which are not soaps. The salts, *e. g.*, NaCl or Na salicylate, may have a thickening action, and the product obtained is transformed to a coherent jelly and vulcanized.

Spongy rubber. H.-F. DE POIX ET CIE. Fr. 708,682, April 4, 1930. Spongy rubber is made by heating a mixt. of rubber and a gas-forming substance in air under pressure, then allowing the gas formed in the mass to expand and finally baking.

Preserving rubber. CHARLES E. BRADLEY and CLAUDE D. MASON (to Mishawaka Rubber and Woolen Mfg. Co.). U. S. 1,832,964, Nov. 24. Paraffin and a mineral wax such as "Casper wax" are applied to rubber articles such as tires or footwear in order to retard "aging."

Preserving rubber. LOUIS H. HOWLAND (to Naugatuck Chemical Co.). U. S. 1,833,021, Nov. 24. See Can. 314,590 (*C. A.* **25**, 5595–6).

Retarding oxidation of organic substances such as rubber. LUDWIG J. CHRISTMANN (to American Cyanamid Co.). U. S. 1,836,702, Dec. 15. About 1% of a compd. such as carbazole or other compd. of like constitution is added as an oxidation inhibitor. Cf. *C. A.* **26**, 625.

Rubber articles. JAMES W. SCHADE and HARLAN L. TRUMBULL (to B. F. Goodrich Co.). U. S. 1,834,974, Dec. 8. A coagulated unvulcanized rubber is plasticized and dispersed in fine particle size in an aq. medium; this dispersion is homogeneously mixed with latex, and the mixt. is used for production of articles by deposition on a form, drying and vulcanizing.

Hollow rubber articles. DOUGLAS F. TWISS and EDWARD A. MURPHY (to Dunlop Rubber Co.). U. S. 1,836,692, Dec. 15. In forming rubber articles such as bulbs or football bladders, a collapsible form is distended and is supported by a collapsible framework, and the form is dipped into an aq. rubber dispersion to form a deposit; the form is removed from the dispersion and the frame is removed from the form, the rubber deposit is dried, and the form is sepd. from the rubber while passing air between the form and the dried rubber deposit.

Apparatus for making rubber articles by immersion. JOHN RUDOLPH GAMMETER. Fr. 708,011, Dec. 3, 1930.

Rubber products. WILLOUGHBY S. SMITH, HENRY J. GARNETT, JOHN N. DEAN, BERNARD J. HABGOOD and HENRY C. CHANNON. Fr. 38,259, Feb. 7, 1930. Addn. to 677,803 (*C. A.* **24**, 3399). A purified rubber suitable for elec. insulators is obtained by submitting the crude rubber to a heat treatment, which may be in water, but not at a temp. above 250°, after which it is treated with a solvent to obtain a fluid soln. which may easily be sepd. from other substances by mech. sepn. In a modification the crude rubber is heated in a solvent under pressure at a temp. of about 200° for a sufficiently long time to reduce the viscosity of the soln., after which the rubber is sepd. from other substances by mech. sepn.

Cured colored rubber products. HANS R. HAERTEL (to Thomas H. Dumper, trustee). U. S. 1,836,660, Dec. 15. In making articles such as colored raincoat material, the rubber is placed in superposed layers, the outer layer contg. color, S and accelerator, and the remaining rubber contg. sufficient ZnO effectively to secure beneficial action of the accelerator in the outer layer during curing of the product.

Rubber conversion products. B. F. GOODRICH CO. Ger. 535,108, April 28, 1926. Thermoplastic products are obtained by treating rubber, at a temp. above 100° and in the absence of S, with a chloride, bromide, or iodide of an amphoteric metal, particularly with $FeCl_3$. The amt. of metal halide may be 10–20%. Examples are given.

Coating surfaces with rubber. DUNLOP RUBBER CO., LTD. Fr. 707,969, Dec. 18, 1930. The products obtained by the direct action of H_2SO_4 or sulfonic acids on gutta-percha, balata, etc., are used as adhesive compns. for joining rubber to hard surfaces.

Coating surfaces with rubber. DUNLOP RUBBER CO., LTD. Fr. 709,816, Jan. 13,

1931. Products obtained by the action of CH_2O or its polymers or derivs. on rubber or ketones or mixts. thereof in the presence of a condensing agent are used for uniting rubber compns., etc., to hard surfaces.

"Jazz-type" color patterns on rubber articles. GEORGE THORNE (to Dunlop Rubber Co.). U. S. 1,832,514, Nov. 17. For producing color "jazz-type" patterns on articles such as rubber shoes, subsequent to their formation from aq. dispersions, a deposit which has been formed and coagulated is introduced into water carrying on its surface bodies of coloring matter in irregular arrangement. App. is described.

Mold with filtering walls, for forming closed hollow bodies from rubber latex. MORGAN & WRIGHT. Ger. 534,850, Feb. 1, 1929.

Calendering rubber. CHARLES C. CADDEN (to B. F. Goodrich Co.). U. S. 1,834,-573, Dec. 1. App. and various details of operation are described.

Composition for lifting friction skin imprints. FRANK K. HADLEY (to St. Louis Rubber Cement Co.). U. S. 1,833,287, Nov. 24. Crepe rubber 25, Guayule rubber 10, carbon black 0.125, Cumar soft rubber 3, cottonseed oil 2 and pine tar 1.5 parts are used together.

Synthetic rubber. I. G. FARBENIND. A.-G. (Erich Konrad and Werner Siefken, inventors). Ger. 537,032, Jan. 17, 1928. Emulsions of rubber-like polymerization products of butadiene hydrocarbons are coagulated by cooling to a temp. below 0°. Examples are given. Cf. *C. A.* **26,** 876.

Rubber substitute. DAVID FALLS (one-half to Frederick W. Haines). U. S. 1,833,941, Dec. 1 A material suitable for molded articles is formed of Irish moss, fullersite, fish glue and formaldehyde.

Oily material suitable for making rubbery products. JULIO T. GIRON. U. S. 1,835,998, Dec. 8. Uncracked petroleum constituents b. about 280–370° under atm. pressure are mixed with at least the aq. portion of the products of fermentation of material such as hay and molasses in water, with aeration in direct sunlight until water is evapd. The material thus prepd. may be treated with $MgCO_3$ and S chloride in tire manuf., etc.

Polmerizing diolefins. GEORG EBERT and FRIEDRICH A. FRIES (to I. G. Farbenind. A.-G.). U. S. 1,832,450, Nov. 17. Polymerization of diolefins such as butadiene is effected in the presence of an alkali metal and of dioxane which serves to facilitate the reaction. Cf. *C. A.* **25,** 2877, 2878.

Condensation products of α,β-substituted acroleins with primary aromatic amines. WALTER KROPP (to I. G. Farbenind. A.-G.). U. S. 1,834,849, Dec. 1. Yellowish to reddish brown oils which are *rubber vulcanization accelerators*, nearly insol. in water but sol. in various org. solvents, are obtained by a process (of which numerous specific examples with details are given) in which α,β-substituted acrolein, in which the α-substituent is an alkyl group and the β-substituent is an alkyl or phenyl group, is reacted upon by a primary aromatic amine such as aniline, *m*- or *p*-toluidine, α-naphthylamine, etc., in the presence of a compd. of an org. or inorg. acid whereby these compds. will probably exert condensing properties. Instead of starting from the aldehydes themselves there may be used such substances as yield the aldehydes during the reaction, such as the oximes of the aldehydes, products having the character of the corresponding aldols, etc. Also it is possible to work in the presence of a suitable org. solvent, such as benzene, toluene, etc.

Artificial gutta-percha. EDUARD S. ALI-COHEN. Ger. 537,034, Sept. 2, 1928. See Brit. 313,373 (*C. A.* **24,** 988).

Rubber vulcanization accelerators. LOUIS H. HOWLAND (to Naugatuck Chemical Co.). U. S. 1,835,050, Dec. 8. Accelerators which function well in rubber stocks contg. a large proportion of carbon black comprise $O[CH_2SC(:S)NR'R'']_2$, such as oxydimethylene dimethyldithiocarbamate or oxydimethylene diethyldithiocarbamate (details of the prepn. of which are given).

Rubber vulcanization accelerator. DUNLOP RUBBER CO., LTD. Fr. 708,819, Jan. 3, 1931. Known accelerators such as mercaptobenzothiazole and dithiocarbamates are condensed with aliphatic radicals substituted by an aromatic ring. Thus, mercaptobenzothiazole is condensed with *p*-nitrobenzyl chloride to produce *p*-nitro-1-benzylthiobenzothiazole. Other examples are given.

Vulcanization accelerators. R. T. VANDERBILT CO., INC. Fr. 708,982, Jan. 8, 1931. Rubber is vulcanized in the presence of an org. compd. of Te which contains the group —CSS—. Compds. having the general formulas $(RR'NCSS)_4Te$, $(ROCSS)_4Te$, or $(\equiv C.CSS)_4Te$, in which R and R′ are hydrocarbon radicals, or RR′N may be piperidyl, etc., are suitable. Examples are given of the use of $(Et_2NCSS)_4Te$.

Accelerating vulcanization. SILESIA VEREIN CHEMISCHE FABRIKEN. Ger. 535,536, May 5, 1926. Vulcanization of synthetic and natural rubber is accelerated by addn. of

salts of alkyl- or arylguanidines with inorg. acids not at the highest stage of oxidation such as HNO_2, H_2SO_3, $H_2S_2O_2$ which form neutral salts with these guanidines. Thus, raw rubber is vulcanized by S, ZnO, and the ditolylguanidine salt of $H_2S_2O_2$ in 30 min. at 3 atm. Further examples are given.

Aniline-crotonaldehyde condensation product. CLAYTON O. NORTH and CHESTER W. CHRISTENSEN (to Rubber Service Laboratories Co.). U. S. 1,832,415, Nov. 17. By the condensation of aniline with more than an equi-mol. proportion of crotonaldehyde (suitably by heating at about 100°) a product is formed which is an *accelerator of rubber vulcanization.*

Selenium dithiophosphates. CHARLES J. ROMIEUX (to American Cyanamid Co.). U. S. 1,836,685, Dec. 15. Compds. such as Se diisopropyl dithiophosphate, etc. (details of the prepn. of which are given) may be used as *rubber vulcanization accelerators.*

Organic disulfides. I. G. FARBENIND. A.-G. (Max Bögemann, inventor). Ger. 535,072, Mar. 1, 1929. Disulfides useful as *vulcanization accelerators* are prepd. by treating mercaptobenzothiazole or its substitution products with aromatic S chlorides or bromides in an org. solvent. Thus, mercaptobenzothiazole may be warmed with *p*-nitrophenyl sulfur chloride in C_6H_6 soln. Other examples are given also.

Schiff's bases derived from α-substituted cinnamylaldehydes. WALTER KROPP (to I. G. Farbenind. A.-G.). U. S. 1,834,850, Dec. 1. Yellowish to reddish brown oils, nearly insol. in water but sol. in org solvents and which are *rubber vulcanization accelerators,* are formed by a process (of which several examples with details are given) in which an α,β-substituted acrolein, in which the β-substituent is an aryl radical and the α-substituent is an alkyl or aryl radical, is reacted upon by a primary aromatic amine as aniline, *m*- or *p*-toluidine, α-naphthylamine, etc., if desired in the presence of a compd. of the group comprising neutral and alk. reacting condensing agents capable of binding water, for example, Na_2SO_4, K_2CO_3, NaOAc or $CaCl_2$. Instead of starting with the aldehydes themselves, there may be used such substances as yield the aldehydes during the reaction, such as the oximes of the aldehydes or products having the character of the corresponding aldols. Also it is possible to work in the presence of a suitable org. solvent, such as benzene, toluene, etc.

Vulcanizing rubber. THE NAUGATUCK CHEMICAL CO. Fr. 708,644, Dec. 31, 1930. Rubber contg. an org. accelerator which is not rendered inactive by NH_3 is vulcanized in the presence of a gaseous medium contg. NH_3. Suitable accelerators include aldehyde-amines, substituted guanidines, polyalkylene, polyamines, thiazols and thiuram sulfides.

Vulcanizing rubber. I. G. FARBENIND. A.-G. (Arthur Beck and Hans Klein, inventors). Ger. 536,383, Nov. 2, 1929. See Fr. 703,791 (*C. A.* **25**, 4742).

Vulcanizing rubber. THE RUBBER SERVICE LABORATORIES CO. Ger. 536,678, Mar. 21, 1928. In vulcanizing rubber, an accelerator formed by condensing the reaction product of butyraldehyde and butylidineamine, with the reaction product of AcH and $PhNH_2$, is used. The AcH may be replaced by other satd. or unsatd. aldehydes such as CH_2O, propionaldehyde, butyraldehyde, etc., or mixts. of these. The $PhNH_2$ also may be replaced by other primary aromatic amines. Examples of vulcanization are given.

"Age-resisting" vulcanized rubber. ROBERT L. SIBLEY (to Rubber Service Laboratories Co.). U. S. 1,836,940, Dec. 15. A mixt. of rubber and S is heated in the presence of an antioxidant comprising a reaction product of an aryl amine with a dihydroxydiaryl halogen-substituted paraffin such as the reaction product of *o*-toluidine with dihydroxydinaphthylchlorobutane.

Utilizing vulcanized scrap rubber. JAMES W. SCHADE and HARLAN L. TRUMBULL (to American Anode, Inc.). U. S. 1,834,973, Dec. 8. The dispersed particles from an aq. dispersion comprising scrap rubber and natural rubber latex are electrodeposited on a deposition base to form sheets, etc.

Rubber, etc. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 709,602, Jan. 17, 1931. Porous or microporous articles are made from aq. dispersions or emulsions of rubber or like substances by adding variable amts. of one or more reagents which are almost without action on the dispersions, and which, by mutual chem. or other reaction, give rise *in situ* to substances which act as coagulants. The reagents are sulfates, chlorides, nitrates and acetates of alkali metals or NH_4 along with oxides and hydrates of bi- and ter-valent metals, or the substances described in Brit. 324,104 (*C. A.* **24,** 3398). The products obtained are vulcanized under such conditions as to avoid evapn. of the liquid contained in the pores or micropores.

Rubber from latex. OTTO AMBROS and ROBERT GRIESSBACH (to I. G. Farbenind. A.-G.). U. S. 1,839,191, Jan. 5. Latex is coagulated by means of an active protease in

the presence of mixts. possessing buffer properties. HCN may be used as an activating agent.

Treating latex. Fritz Günther, Heinrich Hopff and Curt Schuster (to I. G. Farbenind. A.-G.). U. S. 1,838,826, Dec. 29. A Na salt of a butylnaphthalenesulfonic acid or the like is added to latex (suitably in the proportion of about 2%) in order to serve as a stabilizing and preserving agent.

Treatment of latex. Sidney M. Cadwell (to The Dominion Rubber Co., Ltd.). Can. 317,245, Nov. 17, 1931. Rubber latex freed from NH_3 has mixed therewith "oxy normal butyl thiocarbonic acid disulfide," dibenzylamine, ZnO and S in the form of emulsions. The mixt. is allowed to become vulcanized at temp. below 212° F.

Manufacture of rubber articles from latex. Sidney M. Cadwell (to The Dominion Rubber Co., Ltd.). Can. 317,246, Nov. 17, 1931. Latex is vulcanized in the presence of $PhCS_2Na$, S and ZnO at approx. 150°F. and the rubber thus obtained is deposited directly on a porous form in the shape desired to make the article.

Rubber articles. New York Belting & Packing Co. Fr. 709,246, Jan. 13, 1931. See U. S. 1,805,245 (*C. A.* **25**, 3875).

Forming rubber articles such as parts of shoes. Ernest W. Stacey (to United Shoe Machinery Corp.). U. S. 1,838,792, Dec. 29. Mech. features.

Rubber objects. Metallgesellschaft A.-G. Ger. 537,808, Nov. 21, 1926. Solid porous forms are charged with a gaseous coagulation agent, and dipped into rubber latex. In the example the surfaces of the forms are coated with active C or SiO_2 in which HCl is adsorbed as coagulating gas. The forms are then dipped into latex.

Rubber solution. Gai Uyabe and Kenzi Hukunaga (to Huzikura Densen K. K.). Japan. 91,020, April 10, 1931. Unvulcanized rubber is dissolved in a mixt. of naphtha or C_6H_6, EtOH, Me_2CO, and NH_4OH or org. amines.

Electrodeposition of rubber. Wm. A. Williams. U. S. 1,838,241, Dec. 29. In electrodeposition of a vulcanized or unvulcanized latex, NH_4Cl is added in insufficient quantity to cause coagulation and such voltage is applied to the electrodes that the total difference in potential between the electrodes is not greater than sufficient to decompose water. Cf. *C. A.* **25**, 233.

Stabilization of natural or artificial dispersions of rubber. N.-V. de Bataafsche Petroleum Maatschappij and Franz Rudolf Moser. Dutch 23,772, Apr. 15, 1931. Latex preserved with NH_3 is stabilized by addn. of an aq. soln. of an electrolyte (*e. g.*, $AlCl_3$) which will produce a semicolloidal suspension. Per 4 parts latex (0.65% NH_3) 1 part of 4% $AlCl_3$ soln. is used.

Improving properties of rubber. John McGavack (to General Rubber Co.). U. S. 1,840,243, Jan. 5. For improving the properties of rubber in both its raw and vulcanized states, there is incorporated in rubber latex a volatile base soap such as the NH_4 soap of a fatty acid contg. 10–30 C atoms and a volatile base salt such as the NH_4 salt of HCl, HBr, HF, H_3PO_4, HNO_3, H_2SO_3 lactic, oxalic, citric or chloroacetic acids.

Preserving rubber. Sidney M. Cadwell and Sherman I. Strickhouser (to Naugatuck Chemical Co.). U. S. 1,838,034, Dec. 22. Rubber is treated with the product derived from mixing a polyalkylene polyamine such as triethyltrimethylene triamine and a naphthol at temps. not substantially higher than the m. p. of the naphthol.

Retarding aging of rubber. Sidney M. Cadwell and Ludwig Meuser (to Naugatuck Chemical Co.). U. S. 1,839,950, Jan. 5. Prior to vulcanization, there is added to rubber NH_4CNS, dicyanodiamide or other suitable compd. comprising the group $X - C \equiv N$, in which X is an element of the S group and linked to a metal or an org. group (the compd., however, not contg. any metal forming 2 or more stable chlorides).

Antioxidant for rubber. Werner M. Lauter (to Goodyear Tire & Rubber Co.). U. S. 1,838,058, Dec. 22. Rubber is preserved by use of a reaction product of aminoacenaphthene and an aldehyde (such as formaldehyde or benzaldehyde) or formic acid.

Treatment of rubber. Harold E. Cude (to The Dominion Rubber Co., Ltd.). Can. 317,247, Nov. 17, 1931. Comminuted rubber is agitated in the presence of heat with an org. acid capable of forming a water-sol. soap until the mass has assumed a putty-like consistency, the residual acidity is neutralized with a caustic alkali and the heated product is directly mixed with an aq. material to form a dispersion.

Treatment of rubber fiber waste. Reed P. Rose (to the Dominion Rubber Co., Ltd.). Can. 317,248, Nov. 17, 1931. Rubber (100 parts) in broken-up rubber-fiber waste material is treated with 10 parts of a soap-forming fatty acid (oleic, stearic or resin acids) until the rubber component has assumed a plastic, putty-like consistency, 10–15 parts of NaOH in aq. soln. is added for each 100 parts of rubber, and the working continued. The product is finally beaten in an aq. medium contg. an alkali and a protective colloid

(glue, caesin, alginic acid, tannin, soaps, etc.) until the rubber is completely removed from the fiber and in dispersed form.

Apparatus for testing the hardness of yielding materials such as rubber. HARVEY D. GEYER and EDWARD J. DILL (to Inland Mfg. Co.). U. S. 1,839,093, Dec. 29. Mech. features.

Marking rubberized material. CHARLES E. MAYNARD (to Fisk Rubber Co.). U. S. 1,837,461, Dec. 22. Rubber-coated material is marked by displacing the rubber coating while warm according to a desired pattern and to a depth sufficient to impart to the portion so treated the characteristic appearance of the underlying material without completely uncovering the latter. App. is described.

Making inner tubes of rubber. EDWARD FETTER. U. S. 1,840,027, Jan. 5. Various details of app. and operation are described.

Rubber-impregnated gloves. V. ROMBAUTS AND M. STROOBANT. Belg. 375,611, Jan. 31, 1931. The gloves are successively immersed in a series of solns. of increasing concn. contg. rubber, less than 2% S and less than 0.5% of an org. superaccelerator. The solns. are maintained at a max. temp. of 15° during impregnation. The gloves are then vulcanized at a temp. not over 125°.

Apparatus (with a vertical tubular heating chamber) for continuous heat treatment of molded products such as rubber articles. FREDERICK L. CREAGER (to Fairbanks, Morse & Co.). U. S. 1,838,532, Dec. 29. Structural features.

Rubber wringer rolls. HORACE W. THOMPSON (to Lovell Mfg. Co.). U. S. 1,837,925, Dec. 22. A shaft is covered with a rubber wall which at its central portion is formed of a quality of rubber more resilient than the rubber at the ends of the roll, the whole being covered by a rubber envelope of the same quality throughout the length of the roll.

Rendering rubber goods water-resistant. JOHN MCGAVACK (to Naugatuck Chemical Co.). U. S. 1,839,983, Jan. 5. Goods such as sheeting, footwear, surgeons' gloves, etc., are provided with a latex coating and a water-sol. soap is incorporated in the coating while wet and the coating is then further treated with a reagent such as NH_4 alum soln. to effect insolubilization.

Colored coating for rubber and other flexible material. E. COX and C. COX. Belg. 374,310, Nov. 30, 1930. A color mixt. having a casein base and colored with an aniline dye is added to a soln. of shellac in NH_4OH, and an emulsion of latex in borax soln. is added. The rubber is dipped in a C_6H_6 soln. of Para before the coating is applied.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 708,050, Dec. 19, 1930. Emulsions, similar to latex, of polymerization products of 1,3-butadiene or its homologs are coagulated by the addn. of a salt of an alkali metal which forms with the water a noncolloidal soln. Examples are given of the addn. of NaCl, NaOAc, Na_2CO_3 and Na_2HPO_4. Cf. *C. A.* **26,** 876.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 708,807, Jan. 3, 1931. Rubber-like compds. are prepd. by polymerizing diethylene hydrocarbons in the state of an emulsion at a temp. below 20°, preferably with cooling. Polymerization accelerators may be used. The products are sol. in C_6H_6 and have excellent mech. properties. Fr. 708,808 describes the prepn. of similar products by interrupting the polymerization at a pt. when 20–30% of the hydrocarbons is still not polymerized.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 709,637, Jan. 19, 1931. Masses resembling rubber of a high plasticity are made by polymerizing, by the "heat process" or the "emulsion" process, butadiene or its homologs in the presence of unsatd. ketones having the formula $R^1R^2C{:}CR^3COR^4$, in which R^1, R^2 and R^3 are H, alkyl or aryl and R^4 is alkyl or aryl. Examples are given of the use of methylmethyleneethyl ketone, benzalacetone and methylenemethyl ethyl ketone.

Use of sodium hydride to promote polymerization of hydrocarbons of the butadiene series. KARL SCHIRMACHER and LUDWIG VAN ZÜTPHEN (to I. G. Farbenind. A.-G.). U. S. 1,838,234, Dec. 29.

Accelerators for vulcanizing rubber. R. T. VANDERBILT CO., INC. Fr. 709,187, Jan. 12, 1931. S, Te and an org. accelerator are added to rubber before vulcanizing to obtain improved aging qualities. Mercaptobenzothiazole, tetramethylthiuram disulfide and compds. of Se or Te with sulfoacids are suitable accelerators.

Accelerators for vulcanizing rubber. IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 709,420, Jan. 15, 1931. The accelerators consist of a salt of an org. amine along with an org. accelerator of another class, *e. g.*, dibutyl NH_4 oleate or butyl NH_4 acetate and mercaptobenzothiazole or tetramethylthiuram disulfide.

Rubber vulcanization accelerators. JAN TEPPEMA. U. S. 1,838,062, Dec. 22. As vulcanization accelerators, there are used reaction products such as those of 2-chlorobenzothiazole or 2-chloro-6-nitrobenzothiazole with the Na salts of dithiocarbamates

such as Na diethyldithiocarbamate, Na dibenzyldithiocarbamate or Na piperidyldithiocarbamate.

Rubber vulcanization. Clayton O. North (to Rubber Service Laboratories Co.). U. S. 1,838,862, Dec. 29. A deriv. formed by reaction of an aldehyde having less than 8 C atoms such as acetaldehyde, etc., with an α-alkyl-substituted tetrahydroquinoline or the like is used as an accelerator in vulcanizing rubber with S.

Rubber vulcanization. Winfield Scott (to Rubber Service Laboratories Co.). U. S. 1,838,159, Dec. 29. A small proportion of the undecomposed reaction product of cyanogen chloride and Na mercaptobenzothiazole is used with a complementary org. basic accelerator such as diphenylguanidine.

Vulcanization of rubber. Sylvester M. Evans (to the Rubber Service Laboratories Co.). Can. 317,469, Nov. 24, 1931. Rubber is vulcanized by heating rubber and S in the presence of an antioxidant comprising a reaction product of 1 mol. proportion of dihydroxydinaphthyl sulfide and 2 mol. proportions of aniline.

Vulcanization of rubber. Robert L. Sibley (to The Rubber Service Laboratories Co.). Can. 317,470, Nov. 24, 1931. Rubber is vulcanized by heating rubber and S in the presence of an accelerator comprising a product prepd. by the reaction of substantially equimol. proportions of AcH with the reaction product of substantially 1 mol. proportion of 2,4-diaminodiphenylamine and mercaptobenzothiazole.

Assembling and vulcanizing rubber footwear. Henry C. L. Dunker. U. S. 1,838,540, Dec. 29. App. and various details of operation are described.

Latex compound. Ben W. Rowland (to The Goodyear Tire and Rubber Co.) Can. 315,049, Sept. 8, 1931. Tackiness is imparted to the surface of material by applying a coat of latex contg. a small amt. of pine oil.

Compounding rubber latex and pigment. Herbert A. Endres (to The Goodyear Tire and Rubber Co.). Can. 315,052, Sept. 8, 1931. A soap of triethanolamine oleate is introduced into a suspension of pigment. The pigment is filtered and dried and subsequently redispersed in water and the dispersion introduced into latex.

Compounding rubber. Lorin B. Sebrell (to The Goodyear Tire and Rubber Co.). Can. 318,065, Dec. 15, 1931. Into rubber is introduced mercaptobenzothiazole and carbon black that has been activated by heating to 200–900° in a non-oxidizing atm.

Rubber. Technische Chemikalien-Co. G. m. b. H. Ger. 539,366, July 15, 1927. As softeners and anti-agers in the manuf. of rubber goods, use is made of oils obtained by extg. with a solvent, *e. g.*, C_6H_6, the waste waters from low-temp. carbonization and coking processes. Cf. *C. A.* **26**, 1155.

Rubber. I. G. Farbenind. A.-G. Fr. 710,813, Feb. 9, 1931. The aging of natural rubber or masses resembling rubber is diminished by adding to the masses before or after vulcanization 4,4′-dihydroxybiphenyl or its alkyl substitution products.

Rubber. Compagnie française de l'iode et de l'algine. Fr. 711,160, May 15, 1930. Rubber latex is coagulated by the addn. of algine or a deriv. thereof, preferably as a dry powder. The algine, etc., may be added in amt. more than necessary for coagulation to serve as a strengthener.

Rubber. Dunlop Rubber Co., Ltd. Fr. 711,320, Feb. 14, 1931. Rubber compns. which contain a vulcanizing agent such as S, have incorporated therewith vulcanization accelerators obtained by the introduction, by substitution, of a carbalkoxy group into well-known accelerators such as mercaptobenzothiazoles, thiocarbamates and xanthates. Haloformic acid esters are used for the substitution. Examples are given of the prepn. and use of carbethoxybenzothiazole sulfide, carbethoxydiethylaminothioformyl sulfide, carbethoxypiperidinethioformyl sulfide, carbethoxyisopropylthioformyl sulfide and Zn sulfobenzothiazyl. Cf. *C. A.* **25**, 2878.

Rubber. The Naugatuck Chemical Co. Fr. 712,775, Mar. 7, 1931. The phys. properties of rubber, before and after vulcanization, are improved by introducing into a mass of rubber, before vulcanization, a hydrolyzable substance so as to produce acid ions capable of decomposing alkali proteinates and soaps and in amt. sufficient to reduce the p_H value of the aq. ext. of rubber at least to neutral point. The substance introduced may be H_3PO_4, salicylic acid, $CH_2ClCOOH$, $CH_2ClCOONH_4$, $AcONH_4$, $Zn(NO_3)_2$, $ZnCl_2$, etc.

Rubber, etc. I. G. Farbenind. A.-G. Fr. 714,470, Mar. 9, 1931. The products obtained by condensing α-naphthylamine with aliphatic aldehydes contg. 2 or more C atoms, in the presence of alcs. sol. in water and acid, are, after treatment with boiling water, used as protecting agents against the aging of natural and synthetic rubber.

Electrophoretic deposition of rubber. The Anode Rubber Co. (England), Ltd. Ger. 540,489, Mar. 26, 1927. See Brit. 297,780 (*C. A.* **23**, 2850–1).

Rubber dispersible in water. Han'nosuke Honda. Japan. 91,616, June 2, 1931.

Raw rubber is thoroughly mixed with aq. soln. of glue and soap and a solvent of rubber under cooling and then with alk. soln. of casein. The product is dispersible in water.

Rubber composition. SIDNEY M. CADWELL (to Dominion Rubber Co., Ltd.). Can. 318,269, Dec. 22, 1931. With rubber are incorporated therein compounding ingredients including ZnO, S and 2,4-dinitrophenyl dimethyldithiocarbamate, and the compn. is vulcanized in the presence of NH_3.

Composition of calcium silicate and sulfur dioxide suitable for use as a filler in rubber compositions. HERBERT A. ENDRES (to Celite Corp.). U. S. 1,842,394, Jan. 26. Reaction is effected between lime, water and diatomaceous silica by applying heat, and the reaction product is treated with SO_2 gas until the free lime is neutralized.

Silica for use as a pigment or filler in rubber plastics, etc. RAYMOND R. MCCLURE and JOHN W. CHURCH (to Pure Calcium Products Co.). U. S. 1,843,576, Feb. 2. For prepg. silica adapted for use as a "reënforcing pigment" or filler for rubber plastic and plastics contg. drying oils, a liquid such as a colloidal silicic acid soln. is spray-dried to produce finely divided silica, and the silica is then subjected to prolonged attrition while maintaining the size of the particles substantially constant, in order to increase its wettability.

Dyeing rubber. I. G. FARBENIND. A.-G. Fr. 714,167, Apr. 1, 1931. Natural rubber or rubber-like masses are dyed by means of Al lakes of anthraquinone-sulfonic or -carboxylic acids contg. at least 2OH groups, or at least 1OH group or an amino group, substituted or not, and a OH group in the *p*-position. The lakes may be used as they are or mixed with a substratum such as Al_2O_3, lithopone or blanc fixe.

Dyeing rubber mixtures with basic dyes. S. A. BLINKOV, S. I. APEVALKIN and A. G MENGA. Russ. 23,342, Oct. 31, 1931. This method consists in the introduction of the fixative known as "T" into the rubber mixt. together with the product obtained by treating phenol with sulfur.

Rubber hydrohalides. GEORGE OENSLAGER (to B. F. Goodrich Co.). U. S. 1,841,295, Jan. 12. Rubber is converted to a rubber hydrohalide by treatment with a soln. of a H halide such as HCl in a solvent such as EtOAc capable of dissolving substantial proportions of the H halide and of being readily absorbed by rubber but which is substantially a non-solvent of rubber.

Rubber articles. SOCIETÁ ITALIANA PIRELLI. Fr. 712,737, Mar. 6, 1931. Latex which has been vulcanized or mixts. contg. it is used in the processes described in Fr. 651,684 (*C. A.* **23**, 3599), 656,473 (*C. A.* **23**, 4375), 664,844 (*C. A.* **24**, 989), 664,801 and 36,738 (*C. A.* **25**, 1119).

Rubber articles made of thin sheets. ISTVÁN DOROGI, LAJOS DOROGI and DR. DOROGI ÉS TÁRSA GUMMIGYÁR R. T. Hung. 102,824, Sept. 22, 1928. Structural details of manuf. are given.

Rubber-fiber articles. FRANK O. WOODRUFF (to Harry H. Beckwith). U. S. 1,842,706, Jan. 26. A loose mass of unwoven fibers such as cotton treated with dil. HOAc soln. is satd. with an aq. rubber dispersion; excess dispersion is removed from the mass; it is dried, beaten in water to sep. the fibers from each other, and the beaten fibers are formed into desired articles such as shoe soles or automobile tops.

Rubber-fiber products. GEORGE P. F. SMITH and THOMAS G. RICHARDS (to Dispersions Process, Inc.). U. S. 1,841,067, Jan. 12. A compn. suitable for molding or sheeting comprises an aq. dispersion of waterproof binding material such as rubber or asphalt and a loose mass of fibrous material contg. vulcanized rubber, the materials being so proportioned as to give a mass of flowable consistency. Reclaimed scrap material may be used.

Fiber-rubber material suitable for shoe soles. REED P. ROSE and ALLEN F. OWEN (to Mechanical Rubber Co.). U. S. 1,843,581, Feb. 2. An aq. suspension is formed comprising rubber and vegetable fiber, and the rubber is deposited upon the fiber; a relatively thick wet sheet is formed of the material and this sheet is subjected to cold pressing without flowing or spreading it to compact it and remove moisture, and is then dried to not substantially over 15% moisture, and hot pressed.

Thermal treatment of tires and other rubber articles. THE LIQUID CARBONIC CORP. Ger. 538,159, Aug. 27, 1929. Details are given of a method of regulating the pressure in processes in which the treatment is effected in containers with the aid of a heating medium comprising two gases, *e. g.*, CO_2 and steam.

Rubber rings or bands. JOHN R. GAMMETER (to Thermo Process, Inc.). U. S. 1,841,407, Jan. 19. A concd. rubber dispersion is poured on a rotating hot drum to form a tube of rubber with tapered feather-edges; the tube is rolled upon itself from one end to the other to form an endless ring or band, and the band is vulcanized under water at a curing temp. and pressure.

Rubber coatings on articles such as containers, etc. WM. F. ZIMMERLI and WALDO

L. Semon (to B. F. Goodrich Co.). U. S. 1,841,076, Jan. 12. Articles such as containers are coated with an adhesive compn. such as rubber cement and are simultaneously sprayed with a compounded rubber latex and a coagulant (the concn. of the coagulant being so adjusted that the rubber dispersion is coagulated on the surface as a smooth dense layer substantially without flow) and the coating is dried.

Preserving rubber from deterioration. Walter Kropp and Leo Rosenthal (to I. G. Farbenind. A.-G.). U. S. 1,842,989, Jan. 26. Either artificial or natural rubber is treated with an addn. (suitably about 1–5%) of a compd. such as resorcylindan or a similar indanyl phenol.

Retarding oxidation or aging of rubber. Jan Teppema (to Goodyear Tire & Rubber Co.). U. S. 1,841,342, Jan. 12. Vulcanization is effected in the presence of an alkylidene dinaphthol such as methylene di-β-naphthol.

Antioxidant for rubber. William D. Wolfe (to The Goodyear Tire and Rubber Co.). Can. 315,053, Sept. 8, 1931. Rubber is preserved by vulcanization in the presence of aminohydroxyphenyl.

Antioxidant for rubber. Albert M. Clifford (to The Goodyear Tire and Rubber Co.). Can. 315,054, Sept. 8, 1931. Rubber is preserved by vulcanization in the presence of diaminodi-*o*-tolylmethane.

Antioxidant for rubber. Werner M. Lauter (to The Goodyear Tire and Rubber Co.). Can. 316,749, Nov. 3, 1931. Rubber is preserved by vulcanization in the presence of a reaction product of phenyl-β-naphthylamine and S chloride.

Antioxidant for rubber. Albert M. Clifford (to The Goodyear Tire and Rubber Co.). Can. 318,066, Dec. 15, 1931. Rubber is preserved by vulcanization in the presence of a material selected from a group consisting of thioditolylamine, thiodi-β-naphthyl-*p*-phenylenediamine, thio-5-cumidylphenyl or -tolylamine, thio-5-cumidylxylylamine, thio-2,5-diethylphenyl-α- or β-naphthylamine, thio-5,5′-dicumidylamine, thiodixylylamine, thio-4,4′-diaminodiphenylamine, thio-4-hydroxydiphenylamine and thiotolyl-α- or β-naphthylamine.

Rubber antioxidant. Winfield Scott (to The Rubber Service Laboratories Co.). Can. 316,563, Oct. 27, 1931. A vulcanized rubber product possessing age-resisting characteristics is manufd. by incorporating prior to vulcanization a product formed by the reaction of 3.2 parts of S and 18.3 parts of the reaction product of equimol. proportions of acetone and α-naphthylamine.

Antioxidant for rubber. Winfield Scott (to The Rubber Service Laboratories Co.). Can. 316,564, Oct. 27, 1931. Age-resisting vulcanized rubber is manufd. by curing in the presence of a product formed by reaction of 3.2 parts of S on 45 parts of the reaction product of 1100 parts of *p,p*′-diaminodiphenylmethane and 1584 parts of β-naphthol.

Retarding the checking or cracking of rubber materials. Sherman I. Strickhouser (to Naugatuck Chemical Co.). U. S. 1,840,983, Jan. 12. The rubber is treated with an α-diketone such as benzil, phenanthraquinone or furil.

Securing rubber to metal. Clarence M. Carson (to Goodyear Tire & Rubber Co.). U. S. 1,841,322, Jan. 12. In securing rubber to metals, one of the surfaces to be joined is coated with a cement comprising latex, hemoglobin, S and a tanning agent such as formaldehyde or Al sulfate, and the materials are brought into contact and vulcanized together.

Belt dressing composition. John Jensen. U. S. 1,840,815, Jan. 12. Vulcanized rubber is heated to about 200–260° to plasticize it without liquefaction, oil of wintergreen is thoroughly incorporated with the material, and it is allowed to cool to atm. temp.

Waterproofing fibrous materials. Ernst T. Rydberg. Fr. 713,965, Mar. 27, 1931. Fibrous materials are impregnated with a mixt. of vulcanizable oils and S_2Cl_2, the latter in amt. insufficient for complete vulcanization or the complete formation of factice, and then the materials are submitted afresh to the action of S_2Cl_2 to complete the vulcanization or formation of factice in the materials.

Synthetic rubber. I. G. Farbenind. A.-G. Fr. 713,384, Mar. 17, 1931. The addnl. substances necessary for vulcanization are added to the polymerization products of diethylene hydrocarbons when the latter are in the form of a colloidal dispersion and the mixt. is coagulated, *e. g.*, by AcOH. Cf. *C. A.* **26**, 1475.

Polymerization products. I. G. Farbenind. A.-G. Fr. 710,901, Feb. 4, 1931. Derivs. of acrylic acid are emulsified either alone or in admixt. among themselves or with other substances which may be capable of polymerization, and then polymerized in known manner, preferably in the presence of accelerators. The products obtained resemble rubber. A large no. of examples is given.

Recovering rubber. Albert Bray and Jacques Demarquay. Fr. 711,131, May 13, 1930. Rubber is recovered from waste rubber contg. vegetable fibers by hydro-

carbons obtained by pyrogenous distn. of natural or vulcanized rubbers and those derived from copal oil. The swollen rubber is sepd. from the fiber, washed and devulcanized.

Reclamation of rubber and fabric from scrap. Lee T. Smith (to The Hercules Powder Co.). Can. 318,075, Dec. 15, 1931. Scrap contg. rubber and fabric is treated at 100–180° with a mixt. of terpenes b. 160–200°. The fabric is filtered from the solvent, which is distd. off to recover the rubber.

Reclaiming rubber. Taliaferro J. Fairley (one-half each to W. J. Hunter and Mary P. Hunter). U. S. 1,843,216, Feb. 2. The rubber is mixed with a distillate obtained by distg. a terpene wood fraction obtained from the direct distn. of wood in the presence of a clay such as bentonite having a catalytic action, and the mass is heated until the rubber goes into soln., an alkali soln. such as NaOH is added, the solvent is driven off by heating, and the rubber is sepd. from the alkali to obtain a soft rubber mass free from stickiness.

Treating vulcanized rubber for reclaiming, etc. Taliaferro J. Fairley (one-half each to W. J. Hunter and Mary P. Hunter). U. S. 1,843,388, Feb. 2. The rubber is treated with a distillate comprising at least one of the fractions b. below 250° obtained by fractionally distg. turpentine in the presence of a clay having a catalytic action such as bentonite, and the mass is heated until the rubber goes into soln., the soln. is strained and the solvent is driven off and collected.

Rubber treatment. Clifford W. Sanderson (to The Goodyear Tire and Rubber Co.). Can. 316,118, Oct. 13, 1931. Rubber is vulcanized in the presence of an oxidation product of a petroleum hydrocarbon of the paraffin series and an accelerator consisting of mercaptobenzothiazole.

Treating rubber to accelerate vulcanization. Sidney M. Cadwell (to Naugatuck Chemical Co.). U. S. 1,840,932, Jan. 12. There is incorporated with rubber stock a methylated amine resulting from the reaction of formaldehyde and polyethylenepolyamine in an org. acid medium (such as methylated polyethylenepolyamine 1.25%).

Treating rubber to accelerate vulcanization. Sidney M. Cadwell (to Naugatuck Chemical Co.). U. S. 1,843,443, Feb. 2. Rubber is incorporated with (suitably about 0.5–1%) of the reaction product of a polyalkylenepolyamine and an aliphatic aldehyde, such as the heptaldehyde-polyethylenepolyamine reaction product.

Accelerators for vulcanization of rubber. I. G. Farbenind. A.-G. Fr. 38,972, Sept. 3, 1930. Addn. to 691,821 (*C. A.* **25**, 1412). The compds. resulting from the reaction of NH_3 or unsatd. aldehydes are used as their palmitates, stearates, oleates, etc., as accelerators in the vulcanization of rubber. Examples are given of the use of the stearate of tricrotonylidenetetramine.

Vulcanization accelerators. Soc. des usines chimiques Rhône-Poulenc. Fr. 713,928, Mar. 27, 1931. The dithiocarbamic acids formed by reaction of CS_2 on bis-(di-β-β-alkoxyethyl)amines are used as accelerators in the vulcanization of rubber. The products may be represented by the formula $[(RO)_2CH.CH_2]_2N—CS—S—M$, in which R is an alkyl group and M is H, a metal or NH_4.

Vulcanizing rubber. I. G. Farbenind. A.-G. (Eduard Tschunkur, Helmuth Meis and Friedrich Loeblein, inventors). Ger. 540,102, May 7, 1927. A natural or synthetic rubber mix not contg. a vulcanization accelerator is dipped into a warm aq. soln. of a metal dithiocarbamate. Examples are given.

Vulcanizing rubber. The Rubber Service Laboratories Co. Ger. 538,031, Mar. 21, 1928. Vulcanization accelerators are prepd. by sulfurizing the products obtained by the reaction of 2 mols. of butyraldehyde with 1 mol. of a Schiff's base prepd. from butyraldehyde and a primary aromatic amine. Details are given. Cf. *C. A.* **26**, 1158.

Vulcanizing rubber. The Rubber Service Laboratories Co. Fr. 712,878, Mar. 5, 1931. Accelerators are prepd. by condensing an aromatic amine such as 2,4-diaminodiphenylamine with a mercaptoarylthiazole such as mercaptobenzothiazole. The product obtained is mixed with a vulcanization accelerator contg. basic N (*e. g.*, guanidine or an aryl-substituted guanidine). Examples are given. Cf. *C. A.* **26**, 1476.

Vulcanizing rubber. Electric Hose & Rubber Co. Fr. 713,747, Mar. 20, 1931. Rubber products are vulcanized by immersion in a bath composed of a liquid such as an oil or fat capable of heating the products to the necessary temp. without pressure.

Vulcanizing rubber. Società Italiana Pirelli. Fr. 714,443, Feb. 27, 1931. The products obtained by the condensation of dithiocarbamates of secondary bases with aliphatic aldehydes are used as accelerators for the vulcanization of rubber. Such products include (1) methylenedimethylammonium dimethyldithiocarbamate, m. 39–40° (by the reaction of CH_2O on the dimethyldithiocarbamate of dimethylamine), (2) methylenepiperidylammonium piperidyldithiocarbamate, m. 61°, and (3) methyleneethylcyclohexylammonium ethylcyclohexyldithiocarbamate.

Rubber vulcanization. ROGER B. HILL (to The Brown Co.). Can. 316,091, Oct. 13, 1931. Se and an accelerator are added to an aq. rubber dispersion, and the dispersion is heated to effect vulcanization of the dispersed rubber particles without causing coagulation. The Se-vulcanized dispersion, while of lower tensile strength, is tougher than a S-vulcanized dispersion.

Vulcanized rubber. ROBERT L. SIBLEY (to The Rubber Service Laboratories Co.) Can. 316,562, Oct. 27, 1931. A vulcanized rubber product is prepd. by heating rubber and S in the presence of a mixt. of accelerators, comprising 2',4'-dinitrophenyl 2-benzothiazyl sulfide and a reaction product of substantially 3 mols. of butyraldehyde and substantially 1 mol. of aniline.

Vulcanized products. ANTONIO FERRETTI. Fr. 714,799, Apr. 4, 1931. Mineral fibers such as asbestos are reduced to a pulp in a hollander with water, latex is then introduced and coagulated on the fiber and the product is then vulcanized. The coagulating agents may be incorporated with the fibers before the addn. of the latex.

Press for vulcanizing rubber heels. JÁNOS MIHÁLKOVICS. Hung. 102,753, Nov. 20, 1930. Mechanical details.

Apparatus for vulcanizing conveyor and transmission belts, etc. VAOL E. ATKINS (to B. F. Goodrich Co.). U. S. 1,842,646, Jan. 26. Structural and mech. features.

Viscous, pitchy material from pine-tar oil. HERBERT A. WINKELMANN (to Philadelphia Rubber Works Co.). U. S. 1,841,235, Jan. 12. A product suitable for use in rubber compns. is obtained by blowing pine-tar oil with air at an elevated temp. in the presence of a small proportion of S.

Dispersion of lampblack in latex and similar dispersions. C. R. PARK (to Goodyear Tire & Rubber Co.). Brit. 348,174, May 14, 1929. Carbon black or other pigment is rendered more readily dispersible in rubber latex or the like by exposing the pigment particles to vapors such as those of a pine or petroleum distillate, tung oil, soy-bean oil or the like.

Rubber articles. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 715,738, Apr. 20, 1931. Articles are made wholly or in part from aq. dispersions of rubber or like materials, by covering supports or bases with a coagulating agent mixed with substances having wetting properties in the presence of the coagulant, and then covering the supports thus treated with the aq. dispersions referred to. The wetting agent may be casein, glue or saponite and the coagulants may be salts of bi- or ter-valent metals. Cf. *C. A.* **25,** 4443.

Rubber articles. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 715,794, Apr. 21, 1931. The properties of articles made entirely or partly of rubber are improved by making the articles from the concd. latex serum obtained by the final concn. of the scum which comes from the concn. of the latex by centrifuging or from a mixt. of such a serum with aq. compns. or dispersions of rubber. The serum may be used in the form of a powder by drying and pulverizing or as a viscous sirup.

Rubber products. AKT.-GES. METZELER & CO. Ger. 541,305, May 7, 1926. Compns. contg. rubber, factice, S and up to 2% of ZnO, calcd. on the rubber, with or without accelerators and transparent fillers such as glass or mica, are subjected to hot vulcanization. Transparent products are obtained.

Seamless rubber goods. A. P. ARENSBERG and V. A. LEPETOV. Russ. 23,610, Oct. 31, 1931. In the prepn. of thin rubber goods the pattern which is dipped into rubber soln. is first covered with vulcanizing or vulcanization-promoting substances.

Rubber foot-wear. H. C. L. DUNKER. Swed. 70,742, Dec. 2, 1930. Se is used in amts. of 0.5–1.5% in the rubber mixt. Mech. details of the procedure are given.

Rubber derivatives. DUNLOP RUBBER CO., LTD. Fr. 712,646, Mar. 4, 1931. Derivs. of rubber obtained by treating rubber with org. nitroso compds. are used in soln. as *varnishes, lacquers* or a *binding* agent. Thus, rubber is ground up in a mixer and *p*-nitrosodimethylaniline in the form of a base is introduced. The mixt. is left to ripen after mastication. The product is sol. in org. solvents such as C_6H_6.

Stable dispersions of bituminous substances and rubber. N.-V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ. Dutch 25,202, Nov. 16, 1931. Bitumen and rubber dispersions are mixed with addn. of an electrolyte such as $AlCl_3$ or $ZnCl_2$ which will give a finely divided ppt. with KOH present in the dispersion.

Dyeing rubber mixtures with basic dyes. S. I. APEVALKIN, S. A. BLINKOV and A. G. MENGA. Russ. 23,342, Oct. 31, 1931. This method consists in the introduction of the fixative known as "T" into the rubber mixt. together with the product obtained by treating phenol with sulfur.

Coating composition containing dispersed rubber, etc. DUNLOP RUBBER CO., LTD., ANODE RUBBER CO., LTD., E. A. MURPHY, A. NIVEN and D. F. TWISS. Brit. 350,450, March 10, 1930. Compns. for "non-slip" treads of shoes or for mat or rough

finish coatings on various other articles comprise granular dispersions of rubber, etc., such as may be obtained by coagulating aq. dispersions of rubber while stirring, by pptn. *in situ* of compounding ingredients formed by reaction of water-sol. reagents (such as carbonates, sulfates or silicates of the alkali metals or of NH_4) having normally no coagulating effect with subsequently added water-sol. reagents, an ion of which may incidentally possess coagulating properties such as sol. salts of Mg, Al, Ca, Ba or Zn.

Use of bismuth trioxide in rubber compositions as a filler. EVART V. WILLIAMS. U. S. 1,844,306, Feb. 9.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 346,785, Jan. 17, 1930. Latices such as those produced by the polymerization of butadiene or isoprene in emulsions are coagulated by the addn. of salts, preferably in concd. aq. soln., and the emulsifying agent can then be removed by washing. When the initial diolefin emulsions used are formed by the aid of alkylated naphthalenesulfonates or by acid emulsifiers such as the hydrochloride of pentadecyl-μ-glyoxalidine or of the ω-diethylamino-4-ethoxyanilide of oleic acid, the latices cannot be coagulated by acids, but are readily coagulated by salts such as K, Na or NH_4 halides, carbonates, sulfates, nitrates, phosphates, acetates, benzenesulfonates, naphthalenesulfonates, etc. Several examples are given. Cf. *C. A.* **26**, 1476.

Synthetic rubber, etc. STANDARD TELEPHONES & CABLES, LTD., and W. E. HUGH. Brit. 345,939, Dec. 16, 1929. A mixt. of a diolefin such as butadiene, dimethylbutadiene or 2-methyl-2,4-pentadiene and a non-hydrogenated aromatic olefin such as styrene, naphthylethylene, divinylbenzene or their homologs, is polymerized (suitably by heating in an autoclave with a catalyst such as Na or Na amalgam) to form a product resembling rubber or deresinated gutta-percha and which may be used in *insulating submarine cables.* An antioxidant such as phenyl-α- or -β-naphthylamine and a nonvolatile swelling agent such as paraffin may be added and the product may be compounded with natural rubber, etc.

Rubber substitutes. N. V. VEREENIGDE FABRIEKEN VAN STEARINEKAARSEN EN CHEMISCHE PRODUCTEN. Dutch 25,124, Oct. 15, 1931. From oils polymerized according to Dutch patent application 44,643 the free fatty acid is removed by distn., extn. or neutralization. The resulting mass or a mixt. of it with natural rubber is vulcanized.

Rubber substitutes. I. G. FARBENIND. A.-G. Fr. 715,982, April 24, 1931. Masses resembling rubber are made by polymerizing butadiene hydrocarbons in admixt. with one or more compds. of the aliphatic series having a double bond in conjugate position to a triple bond between the atom of C and N and having the formula $R_1R_2C:CR_3CN$ in which R_1, R_2 and R_3 are H or an alkyl, *e. g.*, the nitrile of acrylic acid. Fr. 715,983 describes a similar process in which the compd. of the above formula is replaced by a compd. of the formula $R_1R_2C:CR_3CO_2R_4$ in which R_1, R_2 and R_3 are H or an alkyl group and R_4 is H or a hydrocarbon residue, *e. g.*, acrylic acid or the Me or Bu ester thereof. Cf. *C. A.* **26**, 876.

Rubber-like threads. M. M. SEREBRYANUII. Russ. 23,609, Oct. 31, 1931. Rubber-like threads are prepd. by mixing finely ground fibers and wood with a soln. of rubber in an org. solvent and adding a satd. soln. of NaCl. The mass is then pressed through openings. The mixt. of fibers and wood, after grinding, is mixed with an org. solvent to effect swelling; the operation may be carried out in the cold or in the hot.

Rubber vulcanization accelerators. DUNLOP RUBBER CO., LTD., D. F. TWISS and F. A. JONES. Brit. 346,853, Dec. 23, 1929. Accelerators are prepd. by replacing the H atom of the thiol group of mercaptobenzothiazole by an acyl org. radical such as benzoyl, stearyl or palmityl, as by refluxing a benzene soln. of *p*-nitrobenzoyl chloride and mercaptobenzothiazole. A similar reaction is effected with stearyl chloride. Various modifications of procedure are described.

Tellurium dialkyldithiocarbamates. PAUL I. MURRILL (to R. T. Vanderbilt Co., Inc.). Can. 318,914, Jan. 12, 1932. Na_2TeO_3 (1 mol.) and 6 mols. of acid (HCl) are made to react with 4 mols. of Na dialkyldithiocarbamate with cooling. The compds. formed are valuable vulcanizing agents and accelerators of vulcanization.

Age-resisting vulcanized rubber compound. WINFIELD SCOTT (to The Rubber Service Laboratories Co.). Can. 318,725, Jan. 5, 1932. A rubber compn. is cured in the presence of an antioxidant comprising a reaction product of substantially equimol. proportions of β-naphthol and benzylideneaniline. Cf. *C. A.* **26**, 1158.

Vulcanization of rubber. OSWALD BEHREND (to The Rubber Service Laboratories Co.). Can. 318,724, Jan. 5, 1932. Rubber and S are heated in the presence of a vulcanization accelerator comprising a product prepd. by the reaction of substantially equimol. proportions of the Na deriv. of mercaptobenzothiazole and a chloride deriv.

of a reaction product of substantially 3 mols. of butyraldehyde and 1 mol. of aniline. Cf. *C. A.* **26,** 1476.

Vulcanizing rubber. PAUL I. MURRILL (to R. T. Vanderbilt Co., Inc.). Can. 318,912, Jan. 12, 1932. Rubber is vulcanized in the presence of Te dialkyldithiocarbamate as the vulcanizating agent without the addn. of S.

Vulcanizing rubber. PAUL I. MURRILL (to R. T. Vanderbilt Co., Inc.). Can. 318,913, Jan. 12, 1932. Rubber is vulcanized with the addn. of S as a vulcanizing agent and Te dialkyldithiocarbamate as an accelerator.

Vulcanizing rubber. SOCIETÀ ITALIANA PIRELLI. Fr. 712,418, Mar. 2, 1931. Accelerators for the vulcanization of rubber consist of quaternary di-substituted dithiocarbamates of NH_4 in which the 4H atoms of the NH_4 groups are replaced by 2 residues of an aliphatic aldehyde. Examples of such compds. given include diethylideneammonium dimethyldithiocarbamate prepd. by the action of AcH on NH_4 dimethyldithiocarbamate. Cf. *C. A.* **26,** 1831.

Vulcanizing rubber. P. P. MIKHAILOV. Russ. 23,608, Oct. 31, 1931. As soon as the air pressure in the vulcanizing vessel reaches the required limit, valves are opened consecutively for ventilation purposes while the pressure required by the process is maintained until the vulcanization is finished.

Vulcanizing rubber boots. M. A. PAVLENKO. Russ. 23,607, Oct. 31, 1931. Metal boot trees heated internally by steam or electricity are placed inside of the rubber boots.

Rubber. THE B. F. GOODRICH CO. Ger. 538,941, Dec. 23, 1927. Derivs. of rubber are prepd. by heating the latter with large quantities of PhOH and substances which, with PhOH, liberate strong acids. Examples of the latter substances are rubber chloride, -HCl, -HBr, -2HBr, pinene-HCl and diphenylamine-HCl, -HBr, -H_2SO_4, etc. Cf. *C. A.* **26,** 1156.

Rubber. METALLGESELLSCHAFT A.-G. (Paul Scholz, inventor). Ger. 539,739, July 12, 1927. A reversible concentrate is prepd. from rubber milk or other latex by treating with salicylates and a small quantity of alkali. Thus, rubber latex is treated with 0.25% K salicylate soln. and 0.25% KOH soln. and evapd.

Rubber. SOCIETÀ ITALIANA PIRELLI. Fr. 716,504, May 4, 1931. Rubber, etc., is brought into soln. by heating it with an appropriate solvent under pressure, preferably with stirring, to a temp. above the normal b. p. of the solvent but not above 180°.

Soft and hard rubber. TECHNISCHE CHEMIKALIEN-COMPAGNIE G. M. B. H. Ger. 539,509, July 15, 1927. Addn. to 416,877. In prepg. soft or hard rubber by the method of 416,877, *i. e.*, by treating rubber with unsatd. hydroxylated sulfurized hydrocarbons such as oils obtained from mineral-oil tar and lignite tar by extn. with alc. or acetone, these oils are replaced by oils obtained by extg. tars from coal, shale, peat and wood by dil. oxygenated org. solvents such as alcs., ketones, esters, ethers or mixts. of these. Cf. *C. A.* **26,** 1828.

Rubber articles. SOCIETÀ ITALIANA PIRELLI. Fr. 39,206, June 20, 1930. Addn. to 656,473 (*C. A.* **23,** 4375). The latex is submitted to a moderate heating, *e. g.*, 40–60°, and afterward cooled, *e. g.*, to ordinary temp., before treating it for the formation of the article. Cf. *C. A.* **26,** 1829.

Rubber articles from aqueous dispersions. THE ANODE RUBBER CO. (ENGLAND), LTD. Ger. 542,022, July 25, 1929. See Brit. 317,435 (*C. A.* **24,** 2329).

Colored rubber goods. RUDOLPH KRECH (to I. G. Farbenind. A.-G.). U. S. 1,845,158, Feb. 16. In producing vulcanized colored rubber goods, there is incorporated with the rubber, prior to vulcanization, an insol. metal salt of an acid dye of the triarylmethane dye series having a sulfo group in *o*-position to the methane C atom, such as the Ba salt of "patent blue A." Cf. *C. A.* **26,** 337.

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Vulcanization with Benzoyl Peroxide

I. Contribution to the Knowledge of the Vulcanization Process

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Delft

Three-quarters of a century have passed since the discovery of the vulcanization process by Charles Goodyear, Thomas Hancock, and Alexander Parks without the discovery of an essentially new process of vulcanization. In 1915 Ostromislenski[1] reported the discovery of two new methods of vulcanization, namely, vulcanization with nitrocompounds and vulcanization with peroxides and peracids like benzoyl peroxide.

Ostromislenski was of the opinion that vulcanization is a process which can be divided into two distinct phases,

"Thus we arrive at the conclusion that the vulcanization of caoutchouc is divided sharply into two fundamental phases: 1, a chemical reaction affecting only an insignificant part of the caoutchouc and, 2, adsorption or swelling of the unchanged caoutchouc into the product of this chemical reaction."

a concept which was developed by van Iterson, Jr.,[2] in somewhat different form as a working hypothesis for the vulcanization process.

It is noteworthy that only in 1929 did Ostromislenski[3] publish a second communication on vulcanization with benzoyl peroxide, even then without offering any new theoretical points.

Since Ostromislenski's discovery, vulcanization with benzoyl peroxide has been attributed more than once to an oxidation of the rubber hydrocarbon, *e. g.*, by Twiss.[4] In 1928 Fisher and Gray[5] studied whether the degree of saturation of the rubber changes during vulcanization with benzoyl peroxide. They came to the conclusion that the saturation of rubber is not altered, and therefore it is to be assumed that the vulcanization of rubber does not depend upon a saturation of the double bond of C_5H_8 by oxygen.

In his Colwyn Lecture, Whitby[6] treated the process of vulcanization as a polymerization of raw rubber, and he expressed the belief that benzoyl peroxide plays the same part here as in the polymerization of vinyl acetate, *i. e.*, that of an accelerator of vulcanization.

It is astonishing that in the more than fifteen years which have passed since Ostromislenski's first publication, not a single really detailed study has been devoted to vulcanization with benzoyl peroxide. It seems worth the trouble therefore to investigate this process of vulcanization more closely experimentally, particularly since in the last few years detailed investigations have appeared on the decomposition of benzoyl peroxide under various conditions.

As a starting point, vulcanization with benzoyl peroxide was investigated in relation to the mechanical properties of the vulcanizate. Special attention was paid to the following factors which, as is known, influence vulcanization:

(*a*) Time of vulcanization; (*b*) temperature; (*c*) quantity of benzoyl peroxide; (*d*) accelerator; and (*e*) heat effect of the vulcanization process.

With regard to the technic in general of mixing benzoyl peroxide, there is no difficulty if special attention is paid to two things:

(1) After the raw rubber is plasticized sufficiently, benzoyl peroxide should be mixed in at a low temperature. On a laboratory mill a roll temperature of 50° C. was maintained.

(2) The benzoyl peroxide should be sifted before use so that it will not contain coarse particles which cause porosity and even holes.

All vulcanization experiments were carried out in an oil bath. The tensile tests on the Schopper dynamometer were made in all cases twenty-four hours after vulcanization, with rings of normal size.

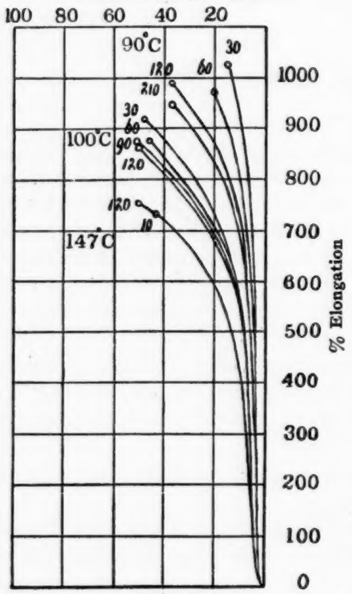


Figure 1

Mixture: first latex crepe 90, benzoyl peroxide 10; vulcanized for increasing times at 147°, 100°, and 90°.

(*a*) and (*b*). Influence of the Time of Vulcanization and the Temperature

A mixture of 90 parts first latex crepe and 10 parts benzoyl peroxide was vulcanized for 10, 20, 30, 60, and 120 min. at 147° C. The results of the mechanical tests are summarized in Table I, and shown graphically in Fig. 1. These results show that at 147° C. the time of vulcanization has only a very slight effect on the mechanical properties, for the position of the stress-strain curve and the modulus at 700% and the tensile strength are approximately the same after 10 and 120 minutes. Therefore vulcanization at 147° C. proceeded relatively rapidly. It should be mentioned in this connection that the tensile strength is very much lower than the optimum tensile strength of rubber-sulfur vulcanizates of the same composition.

Similar experiments were then carried out with the same mixture for increasing times at 100°, 90°, and 80° C.

TABLE I

VULCANIZATION EXPERIMENTS WITH BENZOYL PEROXIDE

Mixture: First latex crepe, 90 parts; benzoyl peroxide, 10 parts

Time of Vulcanization in Min.	Tensile Strength in Kg. per Sq. Cm.	Elongation at Rupture in %	Stress at 700% Stretch	Hardness (Shore Durometer)
Vulcanization at 147° C.				
10	43	735	33	38
20	51	752	35	39
30	50	759	32	40
60	45	736	34	41
120	50	756	32	41
Vulcanization at 100° C.				
30	48	922	16	21
60	46	874	18	25
90	51	877	19	26
120	50	858	21	26

Vulcanization at 90° C.				
30	15	1028	4	21
60	20	975	6	26
120	37	990	8	28
210	37	949	9	30
Vulcanization at 80° C.				
90	9	996	4	23
120	6	755	4	25
150	7	763	4	26
180	6	660	..	27
210	9	748	6	28

The results are all grouped in Table I, and in Fig. 1 the Schopper curves of the vulcanizates at 147°, 100°, and 90° C. are reproduced graphically.

The numbers at the ends of the curves give the times of vulcanization in minutes. At 100° and 90° C. the effect of the vulcanization is no longer independent of the time of vulcanization. Here the curves for the different times do not coincide, instead they take a fan-shaped position, *i. e.*, the stiffness at a given elongation (700%) increases gradually. At 80° C. vulcanization is uncertain as judged by the mechanical properties; even after 210 min. the modulus is still so slight that it is doubtful whether vulcanization has occurred. However, the behavior in benzene indicated that vulcanization had taken place. Though the mixture vulcanized 60 min. at 80° C. dissolved in benzene, the samples vulcanized for a longer time exhibited a marked swelling but did not dissolve. It is therefore safe to say that after 90 min. at 80° vulcanization had taken place.

(*c*) The Quantity of Benzoyl Peroxide

Mixtures were prepared as in Table II, and these were vulcanized for 30 and 60 minutes. Table II gives the results of the vulcanization. These results show that the best tensile properties were obtained with a mixture of 90 parts rubber and 10 parts benzoyl peroxide.

In addition a mixture of 70 parts rubber and 30 parts benzoyl peroxide was vulcanized four hours with the idea of finding out whether a longer vulcanization would lead to hard rubber. However, after four hours the properties had not changed in this direction. This result is therefore in agreement with the statement of Boggs and Blake that this type of vulcanization proceeds only to a state of soft rubber.

TABLE II

INFLUENCE OF THE QUANTITY OF BENZOYL PEROXIDE. VULCANIZATION AT 147° C.

Mixture	Time in Min.	Tensile Strength in Kg. per Sq. Cm.	Elongation at Rupture in %	Stress at 700% Elongation	Hardness (Shore Durometer)
97 parts rubber 3 parts benzoyl peroxide			Not vulcanized		
95 parts rubber	30	39	944	11	32
5 parts benzoyl peroxide	60	40	951	11	36
90 parts rubber	30	50	759	32	40
10 parts benzoyl peroxide	60	45	736	34	41
80 parts rubber	30	4	59	..	46
20 parts benzoyl peroxide	60	5	72	..	48
70 parts rubber	30				
30 parts benzoyl peroxide	60				

(*d*) Accelerator

It was of interest to prove whether vulcanization with benzoyl peroxide is accelerated by the well-known accelerators of sulfur vulcanization. To this end

a few mixtures were prepared from 90 parts rubber and 10 parts benzoyl peroxide with 1 part of the accelerators, diphenylguanidine, hexamethylenetetramine and "quinoidine." These mixtures were vulcanized for 30 and 60 min. at 100° C., along with a blank mixture.

TABLE III

VULCANIZATION WITH BENZOYL PEROXIDE AND ACCELERATOR, VULCANIZATION TEMPERATURE, 100° C.

Mixture	Time of Vulcanization in Min.	Tensile Strength in Kg. per Sq. Cm.	Elongation at Rupture in %	Stress at 700% Elongation	Hardness (Shore Durometer)
90 parts first latex crepe + 10 parts benzoyl peroxide					
	30	48	922	16	21
	60	46	874	18	25
90 parts first latex crepe + 10 parts benzoyl peroxide + 1 part diphenylguanidine					
	30	11	760	7	21
	60	33	924	12	26
90 parts first latex crepe + 10 parts benzoyl peroxide + 1 part hexamethylenetetramine					
	30	40	913	14	30
	60	41	877	17	35
90 parts first latex crepe + 10 parts benzoyl peroxide + 1 part "quinoidine"					
	30	13	568	..	22
	60	15	552	..	28

From the results given in Table III it follows that there is no appreciable acceleration with these substances, in fact the values give the impression that diphenylguanidine and especially "quinoidine" retard vulcanization to a certain extent.[7]

(*e*) Evolution of Heat

Blake[8] maintains that vulcanization proceeds to the soft rubber stage without the evolution of heat, and this point of view was confirmed by him in vulcanization

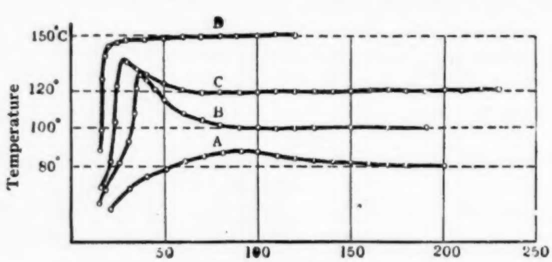


Figure 2—Increase in Temperature in the Middle of a Cylinder of 50 Mm. Diameter during Vulcanization with Benzoyl Peroxide.

Oil bath temperatures: A, 80° C., B, 100° C., C, 120° C., D 150° C.

with *m*-dinitrobenzene and with selenium where only soft rubber is obtained. It was of interest therefore to investigate whether there is any evolution of heat during vulcanization with benzoyl peroxide.

A cylinder of 50 mm. diameter was filled with 90 parts first latex crepe and 10 parts benzoyl peroxide, hermetically sealed, and vulcanized in the oil bath. A thermometer was put in the middle so that the rise in temperature could be read

accurately. These experiments were carried out at 80°, 100°, 120°, and 150° C. The relation between the temperature of the cylinder and the time is shown graphically in Fig. 2.

Without any doubt, these curves show that vulcanization with benzoyl peroxide involves an evolution of heat. Even at 80° C. a rise in temperature occurs which is much greater at 100° and 120°, though it also terminates sooner. It is remarkable that at 150° C. the evolution of heat is entirely consumed in the raising of the temperature of the cylinder to 150°. When this has been reached, the evolution of heat is already ended. It was impossible to determine the quantity of heat evolved by this method; however it was proved conclusively that evolution of heat occurs during vulcanization with benzoyl peroxide, which is apparently contrary to the statement of Blake. One should be very cautious, however, in attributing this evolution of heat to the vulcanization process without further consideration. From the following it will be evident that benzoyl peroxide is completely decomposed during vulcanization, and doubtless this is related to the evolution of heat. It is therefore probable that the evolution of heat during vulcanization with benzoyl peroxide is partly and perhaps wholly caused by the decomposition of benzoyl peroxide and not in the strictest sense by the vulcanization of the rubber. In regard to vulcanization with benzoyl peroxide, it is still an open question whether the statement of Blake is to be regarded as correct.

The Chemistry of Vulcanization with Benzoyl Peroxide

Accordingly it can be concluded from what has been said that benzoyl peroxide undergoes rapid decomposition which is in some way related to the vulcanization of rubber. The question is therefore raised: By what reaction does benzoyl peroxide decompose in rubber and how can one explain this in relation to the vulcanization of rubber?

When a mixture of rubber and benzoyl peroxide is freshly vulcanized the hot sheets are transparent, but they soon become opaque and covered with a layer of fine crystalline needles. Although this has already been observed by Ostromislenski, there is no mention in the literature that these crystals consist of benzoic acid. It seems appropriate therefore to determine quantitatively the quantity of benzoic acid found after vulcanization.

The vulcanizate was extracted with acetone in the ordinary apparatus, and the benzoic acid in the acetone extract was determined by extraction with water and titration with dilute alkali. It is possible that a part of the decomposition products of benzoyl peroxide remained united to the rubber, and therefore the rubber which had been extracted with acetone and swollen in benzene was saponified with alcoholic alkali, and the alcoholic potash extract determined according to the ordinary method. Here, too, benzoic acid was found to be present, and it was determined quantitatively.

Table IV gives the results of analysis of two mixtures, one 90 parts rubber and 10 parts benzoyl peroxide, vulcanized 10, 30, and 60 min. at 147° C.; the other 80 parts rubber and 20 parts benzoyl peroxide, vulcanized 10, 30, and 40 min. at the same temperature.

The analytical data of both mixtures show that vulcanization is ended after ten minutes, and longer times of vulcanization cause no essential changes. In the mixture with ten parts benzoyl peroxide, about six parts benzoic acid were found later, and in the mixture with twenty parts benzoyl peroxide the quantity of benzoic acid was approximately twice as large, *i. e.*, about twelve parts of the mixture.

TABLE IV

VULCANIZATION WITH BENZOYL PEROXIDE AT 147° C.

Mixture: First latex sheet, 90 parts; benzoyl peroxide, 10 parts

	Time of Vulcanization at 147° C. in Minutes		
	10	30	60
Acetone extract	6.8%	6.9%	7.1%
Benzoic acid in acetone extract	3.7	3.8	3.9
Alcoholic alkali extract	3.1	2.7	2.8
Benzoic acid in alcoholic alkali extract	2.2	1.9	2.0
Total benzoic acid	5.9	5.7	5.9
Mixture: First latex crepe 80 parts, benzoyl peroxide 20 parts			
	10	30	40
Acetone extract	10.5%	9.9%	9.8%
Benzoic acid in acetone extract	6.2	6.3	6.4
Alcoholic alkali extract	6.8	6.5	6.4
Benzoic acid in alcoholic alkali extract	5.8	5.6	5.6
Total benzoic acid	12.0	11.9	12.0

When the mixture containing ninety parts rubber and ten parts benzoyl peroxide was vulcanized at 120° C. the result of the chemical analysis was almost the same, as Table V shows. After ten minutes at this temperature, the reaction was still not entirely completed, which was also proved by the reaction with alcoholic potassium iodide solution, for this reaction was feeble after ten minutes of vulcanization. The total quantity of benzoic acid recovered was in this case somewhat higher, *i. e.*, 6.8 per cent based on the mixture.

TABLE V

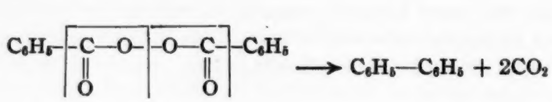
VULCANIZATION WITH BENZOYL PEROXIDE AT 120° C.

Mixture: First latex crepe 90 parts, benzoyl peroxide 10 parts

	Time of Vulcanization at 120° C. in Minutes		
	10	20	30
Acetone extract	7.7%	7.1%	7.0%
Benzoic acid in acetone extract	3.8	3.7	3.7
Alcoholic alkali extract	3.1	3.9	3.8
Benzoic acid in alc. alk. extract	2.2	3.1	3.1
Total benzoic acid	6.0	6.8	6.8
Reaction of benzoyl peroxide with alcoholic KI solution	Very feeble	Negative	Negative

For several years in the organic chemistry Laboratory of the Technische Hochschule in Delft, investigations on the decomposition of diacyl peroxides under various conditions have been carried on by Gelissen, assisted at first by Hermans[9] and later by Reynhart.[10] From these studies on the decomposition of diacylperoxides in general, and benzoyl peroxide in particular, the following reactions were distinguished:

1. Decomposition of benzoyl peroxide by heat, with formation of diphenyl and two molecules of carbon dioxide.



2. Reactions with hydrocarbons according to the R-H scheme, in which two reactions can take place with formation of one molecule of carbon dioxide.

$$C_6H_5-\boxed{\underset{\underset{O}{\|}}{C}-O}-O-\underset{\underset{O}{\|}}{C}-C_6H_5 +$$

$$R{-}H \begin{cases} (1)\ CO_2 + C_6H_5H + C_6H_5COOR \\ (2)\ CO_2 + C_6H_5R + C_6H_5COOH \end{cases}$$

These reactions according to the R-H scheme occur with benzene, toluene, and xylene, as was studied in detail by Gelissen. It was later shown by Overhoff and Tilman[11] that the reaction of benzoyl peroxide with pyridine proceeds exactly in accordance with the R-H scheme.

3. Reactions in which the diacyl peroxides react[12] as mixed acid anhydrides of peracids and acids.

$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-O \,\vdots\, \underset{\underset{O}{\|}}{C}-C_6H_5 + HOH \longrightarrow C_6H_5COOH + C_6H_5COOOH$$

These reactions take place with bases, alcohols, etc.

4. Reactions in which a symmetrical cleavage takes place by the addition of two hydrogen atoms, with formation of two molecules of benzoic acid

$$C_6H_5COO \mid OOCC_6H_5 + 2H \longrightarrow 2C_6H_5COOH$$

These reactions take place with compounds which are able to give up hydrogen atoms and therefore which show a tendency to be dehydrogenated.

The question was therefore according to which scheme the decomposition took place during the vulcanization of rubber. If it was the reaction in Scheme 1 or 2, carbon dioxide would have to be formed in a very considerable quantity. It could be shown by various methods that no trace of carbon dioxide was formed. When the vulcanization was carried out in a tube, and a slow current of nitrogen was passed through and the issuing gas was absorbed in aqueous barium hydroxide, there was no trace of carbon dioxide. Accordingly the decompositions of Schemes 1 and 2 are out of the question. Scheme 3 takes place in alcoholic medium and at normal temperature, and it is therefore a very unlikely reaction in a rubber mixture which contains no water or alcohol.

If the decomposition proceeds as in Scheme 4, a mixture of ninety parts rubber and ten parts benzoyl peroxide should yield 10 per cent benzoic acid, whereas chemical analysis revealed a maximum of only 6.8 per cent. It is therefore clear that this scheme, too, is not acceptable.

There was still to be considered a partial oxidation by the benzoyl peroxide. If the rubber is oxidized, oxidation products are first formed and these can be isolated[13] by extraction with acetone and saponification with alcoholic alkali. With increasing oxidation acetone-soluble products will also be formed.

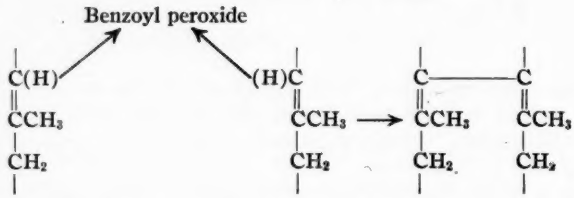
Accordingly with vulcanization the proportion of oxidation products was determined by the method of van Rossem and Dekker. In one case 0.1 per cent and in a second case 0.6 per cent of oxidation products were found. If oxidation occurs, it is very slight in any case.[14]

In short, therefore, it was concluded that none of the schemes fully explains the decomposition during vulcanization with benzoyl peroxide. However, the

impression is that the decomposition proceeds in part according to Scheme 4. Important conclusions are to be drawn from the data at hand.

1. Benzoic acid is formed during vulcanization with benzoyl peroxide, therefore a dehydrogenation of the rubber hydrocarbon takes place.

It is probable that this dehydrogenation occurs with simultaneous bridge formation of two chains $(C_5H_8)_n$ as shown in the following scheme:[15]



It may with good reason be assumed that the benzoyl peroxide acts at the same time as a catalyst of polymerization, therefore polymerization also takes place,

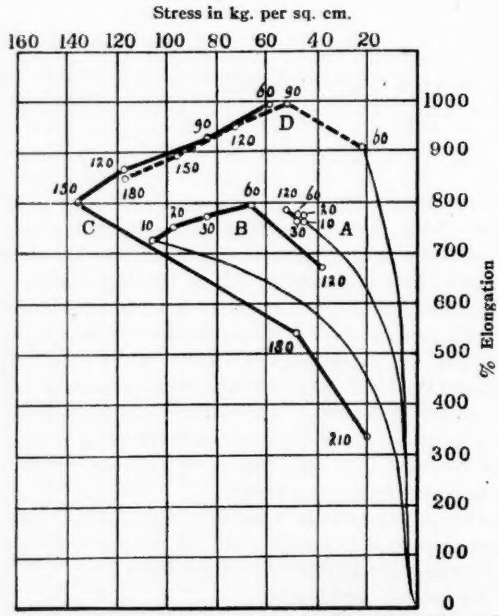


Figure 3—Vulcanization with Benzyol Peroxide and Sulfur Together. Composition of Mixtures A, B, C, and D Shown in Table VI. Numbers on the Curves Are Times in Minutes of Vulcanization at 147° C.

which then might also bring about a bridge formation between neighboring $(C_5H_8)_n$ chains.

The assumption of a bridge formation in part by polymerization, in part by dehydrogenation, appears therefore well founded because this hypothesis offers an explanation of why vulcanized rubber is no longer dissolved. Through a relatively small number of bridge bonds, larger complexes are formed from the rubber

hydrocarbon chains, and these are all insoluble. It should be mentioned that the concept just described applies also to the vulcanization of rubber by sulfur, as has previously been discussed in detail by one of us.[16]

2. It follows from the analysis that part of the benzoic acid is united to the hydrocarbon.

It seems possible that the union takes place where one hydrogen atom is removed by dehydrogenation.

Vulcanization with Benzoyl Peroxide and Sulfur Together

Ostromislenski[17] observed that a very good vulcanization was obtained with a mixture of 100 parts rubber, 10 parts benzoyl peroxide, and 10 parts sulfur. It seemed of interest therefore to carry out a few experiments along this line. Mixtures A, B, C, and D (summarized in Table VI) were vulcanized for increasing times.

The results of mechanical tests of the vulcanizates are shown in Fig. 3.[18] The end point curves of the four series are shown. Mixture B with benzoyl peroxide

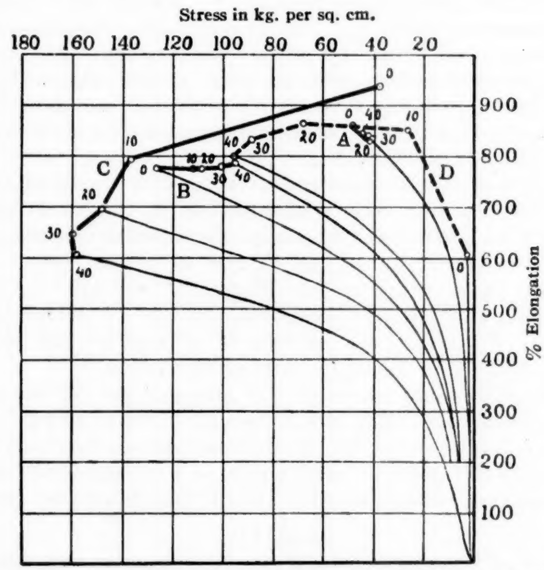


Figure 4—Vulcanization with Benzoyl Peroxide and Sulfur Composition of Mixtures A, B, C, and D Shown in Table VII. Vulcanized 20 Min. at 120° C.; 10, 20, 30, 40 Min. at 147° C.

and sulfur showed a very marked increase in tensile strength compared with A. The optimum was reached after ten minutes, and therefore vulcanization of sulfur seems to be extraordinarily accelerated by benzoyl peroxide. Furthermore Curve B shows a kind of reversion. It was thought that the benzoic acid formed had a detrimental influence, and accordingly a Mixture D was vulcanized in order to determine the effect of benzoic acid. It was found that benzoic acid retards vulcanization with sulfur, but that there is no reversion (D versus C).

It was of interest in this series also to study the combination of sulfur. Accordingly the content of combined S in Mixtures B, C, and D was determined and calculated as the coefficient of vulcanization. Table VI gives the results.

TABLE VI

COMBINATION OF SULFUR IN VULCANIZATION EXPERIMENTS WITH SULFUR AND BENZOYL PEROXIDE

Mixtures	A	B	C	D
First latex crepe	100	100	100	100
Benzoyl peroxide	10	10	...	...
Sulfur	...	10	10	10
Benzoic acid	...	...	...	6

Vulcanization Time in Minutes at 147° C.	Coefficient of Vulcanization of Mixture B	C	D
10	1.6	0.2	...
20	1.8	0.3	...
30	1.9	0.7	...
60	2.5	2.0	1.4
90	...	3.1	2.3
120	3.8	4.4	3.2
150	...	5.6	4.2
180	...	6.8	5.2

It is clearly seen that benzoic acid retards the combination of sulfur, though this combination follows a normal course throughout. On the other hand, Mixture B shows a very abnormal behavior. After vulcanization for ten minutes a considerable combination of sulfur had already taken place. The combination of sulfur was accelerated to an extraordinary degree at the beginning by the benzoyl peroxide. This is completed however at the beginning, and after ten minutes a retardation begins, so that after 120 minutes the combination of sulfur in Mixture C is still greater than that of Mixture B.

Similar experiments were made with a mixture which contained, besides sulfur, diphenylguanidine and zinc oxide. Mixtures A, B, C, and D were prepared (see Table VII for the results), and these were vulcanized at first 20 min. at 120° C. and immediately thereafter for 10, 20, 30, and 40 min. at 147° C., which was readily carried out by the aid of two oil baths at 120° and 147° C.

The idea in mind was that, by vulcanization at 120° C., Mixture C would still be unvulcanized; if therefore the presence of benzoyl peroxide in the mixture accelerates vulcanization it should be particularly evident.

The Schopper end point curves of the mixtures are all shown in Fig. 4. Here again Mixture B has a strong acceleration after 20 min. at 147° C.; however, in the following vulcanization at 147° C. there was again a reversion which cannot be explained by the formation of benzoic acid, as is evident from Curve D. The vulcanization coefficients of Mixtures B, C, and D were determined (see Table VII).

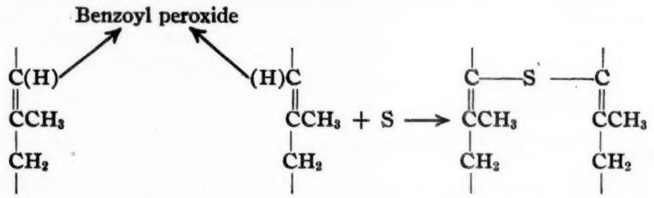
TABLE VII

COMBINATION OF SULFUR IN VULCANIZATION EXPERIMENTS WITH SULFUR AND BENZOYL PEROXIDE

Mixtures	A	B	C	D
First latex crepe	100	100	100	100
Benzoyl peroxide	10	10	...	...
Sulfur	...	5	5	5
Diphenylguanidine	...	1	1	1
Zinc oxide	...	3	3	3
Benzoic acid	...	...	...	5

Time of Vulcanization	Coefficient of Vulcanization B	C	D
20 min. at 120° C.	0.8	0.2	0.2
20 min. at 120° C + 10 min. at 147° C.	1.1	1.2	0.3
20 min. at 120° C + 20 min. at 147° C.	1.4	1.8	0.5
20 min. at 120° C + 30 min. at 147° C.	1.5	2.5	0.9
20 min. at 120° C + 40 min. at 147° C.	1.8	2.9	1.3

These values show again a marked retarding effect of benzoic acid (Mixt. D). The addition of benzoyl peroxide (Mixt. B) brings about a strong acceleration of the combination of sulfur at 120° C., whereas at 147° there is a considerable retardation of the sulfur combination compared to the same mixture without benzoyl peroxide (Mixt. C). The remarkable acceleration of the initial combination of sulfur in the presence of benzoyl peroxide might perhaps be explained by a greater tendency for bridge formation by dehydrogenation with the sulfur taking part, according to the following schematic diagram:



Similar bridge formation in normal sulfur vulcanizates has been assumed by different investigators.[19] Dehydrogenation might therefore have an accelerating effect on sulfur combination.

It was shown in still another way that in rubber that has been vulcanized with benzoyl peroxide subsequent vulcanization with sulfur is possible. Raw rubber was vulcanized with benzoyl peroxide for 20 min. at 120° C., was then masticated on rolls, was extracted with acetone to remove benzoic acid, and a mixture of 100 parts rubber with 5 parts sulfur, 1 part diphenylguanidine and 3 parts zinc oxide, was vulcanized for 10, 20, 30, and 60 min. at 147° C. The results of the tensile tests and the sulfur combination are shown in Table VIII.

TABLE VIII

VULCANIZATION OF RUBBER WITH BENZOYL PEROXIDE AND THEN WITH SULFUR

Mixture: First latex crepe vulcanized with benzoyl peroxide

Milled and extracted	100 parts
Sulfur	5 parts
Diphenylguanidine	1 part
Zinc oxide	3 parts

Time of Vulcanization in Min.	Tensile Strength in Kg. per Sq. Cm.	Elongation at Rupture in %	Hardness (Shore Durometer)	Combined Sulfur
10	16	342	40	0.6
20	20	285	48	1.3
30	21	267	51	1.9
60	27	273	51	3.0

The mechanical properties are bad, which is not surprising in view of the pulverized form of the rubber. However, sulfur combination is quite normal. In this way it was definitely proved that a preliminary vulcanization with benzoyl peroxide does not hinder a subsequent combination with sulfur. Whether the opposite is the case has not been studied.

Aging Tests of Rubber Vulcanized with Benzoyl Peroxide

A few aging tests are described which were made on rubber vulcanized with benzoyl peroxide. A mixture of 90 parts first latex crepe and 10 parts benzoyl peroxide was vulcanized 20 min. at 147° C. and aged in the Geer oven at 70° C. The results are shown in Table IX.

TABLE IX

ACCELERATED AGING TESTS AT 70° C.

Mixture A: First latex crepe 90 parts
Benzoyl peroxide 10 parts

Vulcanized 20 minutes at 147° C.

Time of Heating at 70° C.	Tensile Strength in Kg. per Sq. Cm.	Elongation at Rupture in %	Hardness (Shore Durometer)
Blank	48	706	30
1 × 24 hrs.	11	442	25
2 × 24 hrs.	8	378	25
4 × 24 hrs.	9	413	25

Mixture B: First latex crepe 90 parts
Benzoyl peroxide 10 parts
"Age-rite" 1 part

Vulcanized 20 min. at 147° C.

Time of Heating at 70° C.	Tensile Strength in Kg. per Sq. Cm.	Elongation at Rupture in %	Hardness (Shore Durometer)
Blank	42	841	30
1 × 24 hrs.	45	849	30
3 × 24 hrs.	36	786	29
7 × 24 hrs.	37	795	28
14 × 24 hrs.	30	761	25

Even after 24 hours the decrease in tensile strength was extraordinarily great, and the samples were very sticky. To ascertain whether the temperature of vulcanization had any influence, the same mixture was vulcanized for 20 and 40 min. at 120° C., but the samples showed the same phenomenon. Experiments were then carried out with some antioxidants. Mixtures of rubber 90, benzoyl peroxide 10, "Nonox" 1, or "Age-rite" 1, were vulcanized 20 min. at 147° C. and aged as before at 70° C. "Nonox" gave some improvement and "Age-rite" considerable improvement, as is seen in Table IX.

Finally data were obtained upon the aging at normal temperature of mixtures of rubber 90 parts and benzoyl peroxide 10 parts, which had been cured for different times. The results are shown in Table X.

TABLE X

AGING OF VULCANIZATES WITH BENZOYL PEROXIDE AT NORMAL TEMPERATURE

Mixture: Rubber, 90 parts; benzoyl peroxide, 10 parts

	Tensile Strength in Kg. per Sq. Cm.	Elongation at Rupture in %
Vulcanized 10 min. at 120° C.		
Blank	71	838
After 16 months	20	686
Vulcanized 30 min. at 120° C.		
Blank	52	752
After 16 months	58	775
Vulcanized 20 min. at 147° C.		
Blank	51	752
After 4 months	19	577
Vulcanized 30 min. at 147° C.		
Blank	50	759
After 4 months	34	680

The results are somewhat erratic. A few samples aged well and show without any question better aging than was to be expected after the accelerated aging test; other vulcanizates, on the contrary, deteriorated rapidly at normal temperature. The results are probably affected by factors which are still unknown, such as the natural antioxidants in the rubber and perhaps the preparation of the mixtures.

References

[1] *J. Russian Phys.-Chem. Soc.*, **47**, 1453, 1462. 1467 (1915); translated in *India Rubber J.*, **52**, 467 (1916).

[2] *Meded. Rijksrubberdienst 2nd Serie*, **172** (1916); *Kolloidchem. Beihefte*, **12**, 252 (1920).

[3] *India Rubber World*, **81**, No. 3, 55.

[4] *Trans. Inst. Rubber Industry*, **3**, 398 (1928).

[5] *Ind. Eng. Chem.*, **20**, 294 (1928).

[6] *Trans. Inst. Rubber Industry*, **5**, 184 (1929); **6**, 40 (1930).

[7] We might however warn against the idea that the results obtained with these accelerators are true of all accelerators. Since the time that this paper was presented, results have been obtained which indicate that certain accelerators have considerable influence on vulcanization with benzoyl peroxide. These phenomena will be dealt with at a later time.

[8] *Ind. Eng. Chem.*, **22**, 737 (1930).

[9] Gelissen, "Over Diacylperoxyden, hunne constitutie en hunne beteekenis voor de chemische synthese," *Dissertatie*, Delft, **1926**; Gelissen and Hermans, *Ber.*, **58**, 285, 476, 480, 764, 765, 770, 984, 2396 (1925), **59**, 63 (1926).

[10] Reynhart, "Studies in de chemie der Peroxyden," *Dissertatie*, Delft, **1926**.

[11] *Rec. Trav. Chim. Pays-Bas*, **48**, 993 (1929).

[12] Boeseken and Gelissen, *Verslagen Kon. Ac. van Wetenschappen, Amsterdam*, **24**, 456 (1925).

[13] van Rossem and Dekker, *Kautschuk*, **5**, 13 (1929).

[14] The investigation on the possible oxidation is being continued further.

[15] We might call attention to the fact that we do not particularly choose the hydrogen atom of the double bond, but have taken this simply as an example.

[16] In an address before the London Section of the Institution of Rubber Industry on "Vulcanization with and without Sulphur" which will be published shortly.

[17] *India Rubber World*, **81**, No. 3, 55.

[18] For brevity the tables are omitted which contain the values of the physical tests.

[19] C. O. Weber, *The Chemistry of India Rubber*.

[Translated from Kautschuk, Vol. 7, No. 7, pages 128–132, July, 1931.]

New Condensation Products of Rubber Hydrocarbons by the Aid of Benzyl Chloride

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A. Preparation and Properties

The application of the long-known Friedel-Crafts reaction to rubber hydrocarbons led to a new type of condensation products which may be called provisionally *aral cyclorubbers* ("benzylidene rubbers"), since their benzylidene groups are probably condensed with the polyprene skeleton to cyclic systems.

It would not have been foreseen without further work that rubber would form this type of condensation product with aral halides in the presence of aluminum chloride, since on the one hand benzyl chloride is known to form, by the action of aluminum chloride in the Friedel-Crafts[1] reaction, an amorphous, apparently high molecular hydrocarbon of the empirical composition $(C_7H_6)_x$, and on the other hand rubber in solution is transformed by the metal chlorides,[2] especially aluminum chloride,[3] into amorphous polycyclorubbers.

Under definite conditions of condensation with aluminum chloride aral groups are combined with the skeleton of the rubber hydrocarbon with the formation of white to yellowish amorphous bodies which contain, in addition to a small proportion of organically combined chlorine, only carbon and hydrogen, and are therefore to be regarded as hydrocarbons. In their physical and chemical properties these substances resemble the already known amorphous substance of the empirical formula $(C_7H_6)_x$, which doubtless is polybenzylidene, probably hexabenzylidene.

The reaction is carried out by pouring the anhydrous aluminum chloride in carbon tetrachloride quickly into a cooled rubber-carbon tetrachloride-benzylchloride solution. There is an energetic evolution of hydrochloric acid and a gray-white spongy mass is formed, which remains as a brittle, white, amorphous product. After hydrochloric acid is no longer evolved on the boiling water bath, the carbon tetrachloride is distilled away, and the excess benzyl chloride is removed by acetone extraction. If, on the other hand, benzyl chloride is added dropwise to the solution of rubber in carbon tetrachloride containing the aluminum chloride in suspension, a red-brown mass is formed which turns black-brown on heating. Upon cooling the reaction mixture, there is formed above a dark brown solution a hard, brown crust, which after extraction with acetone and pulverization is a yellow-brown powder, which shows all the reactions of the cyclorubber of Bruson (*loc. cit.*). In the latter case it seems as if the cyclicization of the rubber hydrocarbon by aluminum chloride, which takes place very slowly at ordinary temperature, has been accelerated by the benzyl chloride and the free hydrochloric acid liberated from the aluminum chloride, so that a true transposition of the hydrocarbon with benzyl chloride no longer takes place.

It was observed in addition that the quantity of the reaction products obtained under otherwise similar conditions seemed to depend very much upon the concentration of the rubber and upon the degree of polymerization of this colloid.

Thus in Experiment 3 (see Table I) with the highest concentration of rubber and approximately the same excess of benzyl chloride, the yield was lowest in spite of double the quantity of aluminum chloride, as in Experiment 2. This low yield was also probably due in part to the fact that the plantation crepe (used in all the experiments) was in this case masticated only a short time and after swelling in carbon tetrachloride was kept at the boiling point of this solvent (78° C.) for only four hours, whereas in the other experiments, with the exception of 2 and 7, rubber of only one-tenth as great concentration was used and the rubber was more highly masticated and was maintained at the above temperature about twice as long. In Experiment 7 undercured rubber was used. Since in this case there was no solution, but only a swelling of the colloid, the calculated concentration of rubber is in reality about ten times too high. Therefore, in spite of the great excess of benzyl chloride, a yield only about as great as the yields in Experiments 2 and 3 was obtained.

TABLE I

DEPENDENCE OF THE COURSE OF THE REACTION BETWEEN THE RUBBER HYDROCARBON AND BENZYL CHLORIDE ON THE CONCENTRATION OF THE COMPONENTS

No. of Experiment	Rubber Hydrocarbon Used (G.)	Quantity of CCl_4 (Cc.)	Concentration of Rubber Hydrocarbon in Liquid Phase (Vol.-%)	Benzyl Chloride Used (G.)	Corresponding C_7H_6	$AlCl_3$ Used (G.)	Quantity Reaction (G.)	of Solid Product (%)	Ratio $C_5H_8:C_6H_6$ in the Reaction Product
1	2	80	2	22*	15.7	5	12	72	1:4
2	10.5	350	23	110*	78.5	...	42	47	1:2.2
3[1]	22.3	525	35.6	110**	75	2	30.5	30	1:1
4	2.5	75	2.5	27*	19.3	1	20	92	1:5
5	2.5	75	2.7	15.5*	11	1	12.5	92	1:3
6	2.5	75	2.7	15.1*	10.7	2	12.6	95.5	1:3
7[2]	10	300	2.5	110**	75	2	50	86	1:3
8[3]	1	50	2	11*	7.8	0.5	1.8	...	1:1
9	...	20[4]	...	22*	15.7	0.5	15.2	97	...
10	...	25[5]	...	22*	15.7	1	15.0	97	...

* Chemically pure.
** Technically pure.
[1] Slightly masticated and heated for a short time at 78° C.
[2] Under-cured rubber, very finely ground and swollen 24 hours in CCl_4.
[3] Purest Tjipetir gutta-percha.
[4] Reaction at ordinary temperature carried out to the end (16 hrs.)
[5] Reaction at 80° C. carried out to the end (4 hrs.).

Since in this reaction the rubber hydrocarbon is transformed quantitatively into the condensation product, it is possible to obtain with fair precision from the yields the proportion of rubber hydrocarbon and benzylidene residue, C_7H_6, in the solid reaction products. In this way it was found that with low concentrations of rubber there were stoichiometric relations between the two constituents which ranged from 1:3 to 1:5. These ratios support the opinion of the author that in this case true chemical combinations appear to have taken place between the rubber hydrocarbon and aral groups. The influence of the concentration of the rubber and its degree of polymerization on the course of the reaction is already known from other reactions of these colloids, *e. g.*, hydrogenation experiments by Harries, Pummerer, Staudinger, and their co-workers.

As far as the properties of the new condensation product (called "benzylidene rubbers" for short) are concerned, it might be mentioned that they are white to slightly yellow amorphous substances which can be pulverized with extraordinary

ease. They have a density of about 1.10, hardly swell in organic solvents, and in fact are almost insoluble. In the reactions above there are also formed to a greater or less extent acetone-soluble and benzene-soluble, yellow resinous products (*e. g.*, in Experiment 9 about 30% which melts at 70° to 71° C.), whose proportions appear to depend upon the temperature of the reaction and the amount of solvent (aluminum chloride). They have not been investigated further.[4] Upon heating to 100° C., the insoluble substances show slight thermoplasticity which is manifest in a slight agglomeration under pressure. From the chemical point of view they are very inert toward halogens and oxygen, which may be a result of their chemical saturation, in contrast to cyclorubbers which still show 20 to 30% of unsaturated bonds. The acetone-extracted products still contain small quantities of organically combined chlorine (0.5 to 3%), which can be almost completely removed by boiling with aniline. On treatment with bromine carbon tetrachloride solution, bromine is taken up by substitution, and the color disappears very slowly with evolution of hydrobromic acid. Between 1.6 and 3.2% of bromine were found after twenty-four hours.

TABLE II

LUMINESCENT COLORS OF THE HYDROCARBONS $(C_7H_6)_x$ AND $(C_{26}H_{26})_x$ COMPARED WITH ALLIED HYDROCARBONS

Substance	State of Aggregation	Luminescent Colors in Filtered Ultra-violet Light from Mercury Lamp	Spectroscopic Behavior of Luminescent Light within Visible Range
Benzyl chloride	Liquid	Very pale violet	....
$(C_7H_6)_x$	Solid	Very bright light blue	No absorption bands
$(C_{26}H_{26})_x$	Solid	Strong light violet	No absorption bands
Fluorene	Solid	Intense deep violet	Distinct absorption bands in green, blue, and violet
Phenanthrene	Solid	Bright blue-green	Weak absorption bands in gold and green
Retene	Solid	Strong deep violet	Extremely weak absorption bands in gold and green
Heat transformation product of $(C_7H_6)_x$	In benzene	Bright blue-green	Very weak absorption bands
Heat transformation product of $(C_{26}H_{26})_x$	In benzene	Bright light green	Very weak absorption bands

With stronger heating the hydrocarbon sinters and turns yellow at about 180° C., whereas the substance $(C_7H_6)_x$ on rapid heating at about 320° to 340° C. melts with blackening and incipient decomposition; the "benzylidene rubbers" change at this temperature into a spongy product with strong sintering and blackening. The former can be ground to a yellowish brown powder which resembles the hydrocarbon known as cuprene[5] of the same empirical composition $(C_7H_6)_x$ which is formed from acetylene and copper at 180° C., this last a dark brown powder. These brown conversion products are about 50% soluble in acetone and benzene with yellow or red-brown colors, whereas they are much less soluble in benzine.[6] The benzene solutions show a distinctly green fluorescence in daylight (somewhat like solutions of anthracene), while in filtered ultra-violet light from the mercury lamp the solutions of the light brown substances are an intense blue-green and those of the dark brown substances are bright green, of about the color and intensity of phenanthrenes. These results are in accord with those of Perkin and Hodgekinson[7] who were able to detect anthracene as well as toluene in the distillation of the substance $(C_7H_6)_x$ and permit certain conclusions regarding the constitution of the new hydrocarbon.

Like the heat-conversion products, the original hydrocarbon shows in filtered ultra-violet light an intense luminescence, which in color and intensity is like that

of fluorene (see Table II). While the hydrocarbon $(C_7H_6)_x$ is bright blue, the benzylidenerubbers appear bright violet, a proof that strongly fluorophoric groups or bonds must be present in both systems. In distinction to the otherwise identical fluorescent light of fluorene, the luminescent spectrum of the benzylidenerubbers shows no absorption bands in the visible range. In contrast to the hydrocarbons mentioned, the cyclorubbers of Bruson show only an extremely weak yellow-brown luminescence, and therefore they possess no fluorophore. There may, however, be some doubt whether these "benzylidenerubbers" might not be mixtures of the cyclorubbers of Bruson with the amorphous substance $(C_7H_6)_x$. However, there should be no such doubt, because of the characteristic behavior of these substances with concentrated sulfuric acid at its boiling point (280° C.). Whereas under these conditions the benzylidenerubbers and the substance $(C_7H_6)_x$ as well as the sulfuric acid undergo no appreciable change with longer heating, all the cyclorubbers become red-brown or black, and the acid is also colored an intense yellow to brown. A similar behavior is found with boiling carbon tetrachloride and acetic acid (boiling point, 154° C.), in which the cyclorubber dissolves with a deep red to brown color, whereas the new hydrocarbon shows no change.[8]

B. Elementary Analysis and Heat of Combustion of the Substance $(C_7H_6)_x$ and of "Benzylidenerubber" According to Experiment 5

The condensation products described above yielded the values for heats of combustion given in Table III after many hours' extraction with boiling alcohol and acetone, drying *in vacuo* and combustion in the Mahler-Kröcker bomb. With

TABLE III

ELEMENTARY ANALYSIS AND HEAT OF COMBUSTION OF THE CONDENSATION PRODUCTS $(C_7H_6)_x$ AND OF "BENZYLIDENERUBBER" (ACCORDING TO EXPERIMENT 5)

I. Condensation product $(C_7H_6)_x$

(*a*) Heat of combustion (constant volume)

(corrected temperature)		
1. 0.7226 grams substance	2.430° C.	9530 g.-cal.
2. 0.5846 grams substance	2.012° C.	9560 g.-cal.
for C + H = 100%	calculated	9620 g.-cal.

(*b*) Elementary analysis of 2

1.9940 CO_2	0.5437 C	= 93.0% C
0.3300 H_2O	0.0367 H	= 6.3% H
0.4950 substance	0.010 AgCl	= 0.5% Cl*
0.8074 substance	0.002 Al_2O_3	= 0.25% Al_2O_3

II. (*a*) Heat of combustion of "benzylidenerubber" according to Expt. 5.

(corrected temperature of heating)		
1. 0.6370 grams substance	2.163° C.	9433 g.-cal.
2. 0.5860 grams substance	1.990° C.	9440 g.-cal.
3. 0.5790 grams substance	1.958° C.	9410 g.-cal.
for C + H = 100%	calculated	9500 g.-cal.

(*b*) Elementary analysis of "benzylidenerubber" according to Expt. 5.

1. 2.1090 CO_2	0.5753 C	90.80% C
0.4156 H_2O	0.0462 H	7.25% H
2. 1.9584 CO_2	0.5341 C	91.15% C
0.3924 H_2O	0.4140 H	7.07% H
3. 1.9340 CO_2	0.5275 C	91.10% C
0.3666 H_2O	0.0407 H	7.03% H
0.6910 substance	0.0450 AgCl	1.61% Cl*
0.3430 substance	0.0225 AgCl	1.62% Cl
0.5068 substance	0.0006 Al_2O_3	0.10% Al_2O_3

for C + H = 100% calculated C 92.8 %, H 7.2%

$C_{26}H_{26}$ = 100% calculated C 92.75%, H 7.25%

* Obtained by melting the original substance with Na_2O_2, Na_2CO_3.

the pure substances (C + H = 100%) a heat of combustion of 865 cal. was calculated for a C_7H_6 group of the substance $(C_7H_6)_x$. From the elements a value of 851 cal. was calculated, so that the heat of combustion for the C_7H_6 group is 14 cal. For one-half mol. of the isomer stilbene, values between 883 and 886 cal. were found. It is thus seen that no ethylene bonds can be present in the above substance.

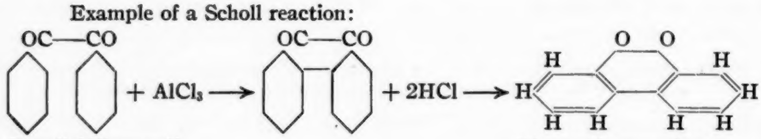
TABLE IV

PROBABLE CONSTITUTION OF THE HYDROCARBONS INVESTIGATED

(*a*) The substance $(C_7H_6)_x$ and its heat-conversion products

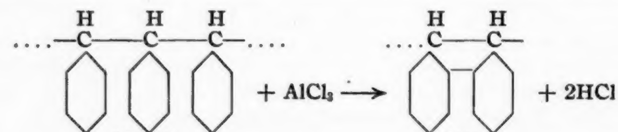
1. $2C_6H_5CH_2Cl + AlCl_3 \longrightarrow C_6H_5CH_2CHClC_6H_5$ (I) + HCl
   Dibenzylchloride
2. $xC_6H_5CH_2CHClC_6H_5 + yC_6H_5CH_2Cl \longrightarrow xC_6H_5CH_2(CHC_6H_5)_xCHClC_6H_5$ (II)
3. $C_6H_5CH_2(CHC_6H_5)_4CHClC_6H_5 \longrightarrow [C_6H_5CH]_6$ (III) + HCl
   Hexabenzylidene or hexaphenylhexahydrobenzene

Example of a Scholl reaction:



Benzil (dibenzoyl) Phenanthrenequinone

4.

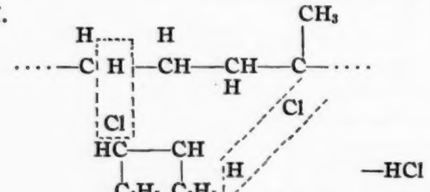


$(C_7H_6)_x$ (IV)

$(C_{14}H_{10})_x$ (Phenanthrene complex)

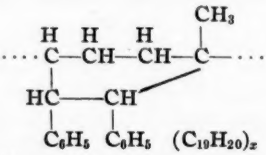
(*b*) The substance $(C_{19}H_{20})_x$ ("benzylidenerubber") and its homologs

I.



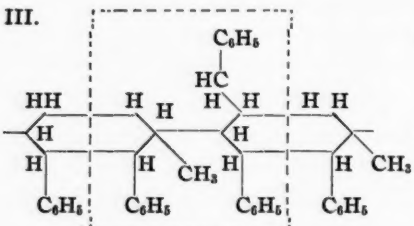
Hydrochlororubber + dibenzylchloride

II.



Methyldiphenylpolyhexahydrobenzene

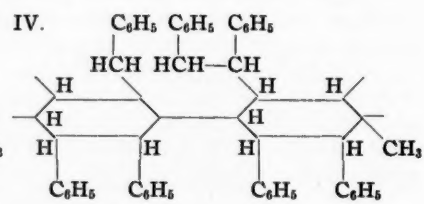
III.



$(C_{26}H_{26})_x$

Methyldiphenylbenzylhexahydrobenzene

IV.



(Experiment 4)

Methyldiphenyltribenzylhexahydrobenzene

Based on C + H = 100%, the heat of combustion of benzylidenerubber has a calculated value in Experiment 5 of 9500 cal. Based on the course of the reaction in this and several other experiments, according to which there are three (C_7H_6) groups for every isopentene group for the simplest theoretical molecule of this substance, a heat of combustion of 3190 cal. and a heat of formation of 132 cal. are calculated.

If in the reaction product there is a mixture of cyclorubber and the substance $(C_7H_6)_x$ in the proportion of 1:3, then in an analogous way the calculated heat of combustion is 3266 cal. which is about 75 cal. higher than the experimental value.[9]

The quantitative determination of the combustion products led in the case of the condensation product of benzyl chloride to a C:H ratio which agreed very well with the empirical formula $(C_7H_6)_x$. In the case of "benzylidenerubber" (Expt. 5) this ratio gives the simplest formula $C_{26}H_{26}$, which would correspond to the ratio of one isopentene residue to three benzylidene residues.

C. Probable Constitution of the Hydrocarbons Studied

In the attempt to draw conclusions about the constitution of the new hydrocarbons many difficulties arose which are principally due to the high polymeric amorphous nature of these substances. For the time being, therefore, the author has resorted to conclusions based upon analogy, and the constitutional formulas can be considered only as working hypotheses.

Above all it is necessary to establish the constitution of the substance $(C_7H_6)_x$. Dibenzyl chloride is probably the simplest reaction product of benzyl chloride and aluminum chloride, and this compound appears to lead to further analogous condensations which in turn must lead to substances of the form: (*a*) (II) in Table (IV). There must be considered as an additional phase the closing of the ring between the CH_2-group of the first and the CHCl-group of the last member, with splitting off of hydrochloric acid, which would probably form six rings, according to the general manner of formation of hydroaromatic hydrocarbons.[10] Molecular weight determinations would show the existence of such a substance as $(C_7H_6)_6$ (hexabenzylidene or hexaphenylhexahydrobenzene and hexaphenylcyclohexane).

The assumption of the existence of the adjacent benzylidene complexes finds support in the transposition products of the phenanthrene type. As is easily seen the Scholl reaction between two adjacent phenyl groups actually leads to phenanthrene (*a* in Table 4), which is wholly analogous to the transposition which has been observed in the case of benzyl (dibenzoyl) to phenanthrene quinone[11] when fused with aluminum chloride.

It is more difficult to explain the constitution of "benzylidenerubbers" than that of the substances from benzyl chloride. Obviously here one is dealing with reactions of the dibenzyl chloride first formed with the hydrochlororubber formed by splitting off of hydrochloric acid, as shown in 4–1 (Table IV). Since the tertiary united chlorine atom of the hydrochlororubber is very reactive there is a very great tendency to cyclicization[12] which may lead to configurations as in II (Experiment 2) (methyldiphenylpolyhexahydrobenzene). The methylene groups of the latter are able, under the influence of aluminum chloride, to react with additional molecules of benzyl chloride and dibenzyl chloride.[13]

Taking into consideration the substance with three benzylidene residues, we obtained the compound III (benzyldiphenylpolyhexahydrobenzene), in which the complex $C_{26}H_{26}$ is repeated, and which would correspond very well to the empirical formula found experimentally.[14] Further substitution by a dibenzyl residue might give a substance IV, which perhaps is present in the reaction product of

Experiment 4 (Table I). The transposition by heat might here, too, lead to phenanthrene-like complexes, as in previous cases.

The great chemical and thermal stability and low thermoplasticity under pressure may permit a practical use of these interesting condensation products as acid-proof insulating materials.

References

[1] *Bull. Soc. chim.*, **2**, 43, 53; Radziewanowski, *Ber.*, **27**, 3237.

[2] Bruson and collaborators, *Ind. Eng. Chem.*, **19**, 1033 (1927).

[3] *English Patent* 320,427 (1928); *U. S.* 1,751,817 (1930).

[4] These acetone-soluble portions also have luminescence of the same color but of less intensity than the insoluble condensation products.

[5] Mailhe, *Chem.-Ztg.*, **29**, 464.

[6] The relative solubility of anthracene oil in the solvents mentioned is quite analogous.

[7] *J. Soc. Chem. Ind.*, **37**, 726; Schramm, *Ber.*, **26**, 1706.

[8] Kirchhof, *Kautschuk*, **4**, 24 (1928).

[9] Kirchhof and Matulke (*Ber.*, **57**, 266 (1924)) found the heat of combustion of sulfuric acid-cyclorubber to be between 1339 and 1346 cal. per molecule of $C_{10}H_{16}$, or 670 cal. per molecule of C_5H_8.

[10] *Ann.*, **278**, 110; *Ber.*, **34**, 2799.

[11] Scholl and Schwarzer, *Ber.*, **55**, 324 (1922).

[12] Staudinger, *Kautschuk*, **1**, 6 (1925).

[13] It is seen that here there is a completely analogous base complex as in the case of hexabenzylidene, which also gives a basis for the group term "benzylidenerubbers," whose somewhat different colored and feebler luminescence in ultra-violet light is perhaps attributable to the smaller number of phenyl groups. These relations might be explained by the Raman effect. Mention should be made at this time of the general importance of this new effect in explaining the problem of the chemical constitution, especially in connection with the rubber hydrocarbon and related substances.

[14] Theoretically the substance in Experiment 5 corresponds to a formula $C_{26}H_{24}$. This led to the assumption that there was the formation of a 5-ring system analogous to the Scholl reaction (between the carbon atoms in (1) (Table IV–VI, III and the CH-residue of the benzyl group), whereby hydrofluorene would be formed. This assumption appears for the moment too uncertain.

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The Nature of Vulcanization

Part IV (Continued)

H. P. Stevens and W. H. Stevens

In a previous communication[1] the authors have discussed the limiting figure for combined sulfur in vulcanized rubber, and shown that under suitable circumstances the coefficient of vulcanization can exceed the figure of 47, which is that required by the formula C_5H_8S. It was thought that the combined sulfur in excess of this amount resulted from the substitution of sulfur for hydrogen. (Further information on this point will be found in the second part of this paper.)

In the course of these experiments[1] use was made of the ether-hydrochloric acid extraction method[2] for the removal of mineral sulfides in soft vulcanized rubber. It was thought that this extraction method might not be suitable for use with vulcanites, since the amount of swelling produced by the ether was relatively inappreciable, and consequently the metallic sulfides were not necessarily decomposed. It was also thought that the acid mixture might react with a part of the rubber sulfide and result in a lower coefficient, which would depend on the time of extraction. It is known that vulcanite can be decomposed by the action of alcoholic potash, and the combined sulfur has been reduced in some cases to 26 per cent.[3] It is reasonable to suppose that decomposition takes place in the presence of concentrated hydrochloric acid.

In order to determine the extent to which the sulfide is decomposed by the action of the acid a series of extractions was made.

The vulcanite employed was made on our formula No. 7 as previously used, *i. e.*, rubber 100, sulfur 200, zinc oxide 20, zinc diethyldithiocarbamate 20, and this was vulcanized for 168 hours at 100°. The material was extracted with acetone before and after ether-hydrochloric acid extraction. The coefficients obtained are shown in the following table:

	Duration of 1st Acetone Extn., Hrs.	Duration of Ether-HCl Extn., Hrs.	Duration of 2nd Acetone Extn., Hrs.	Combined Sulfur %	Coefficient of Vulcn.	Ash, %
1 (unextracted)	..	..	..	..	..	7.99
2	90	..	32	41.6	91.4	12.90
3	90	615	32	38.1	63.4	1.80
4	90	1000	32	35.5	58.1	1.25
5	90	2000	32	34.2	52.4	1.08

These results show that: (1) The sulfides of rubber are slowly decomposed by the extraction mixture, but the combined sulfur at the end of the operation is still in excess of that required for the formula C_5H_8S. To judge from the gradual reduction of the proportion of combined sulfur it is quite possible that it is tending to 47 per cent as a limiting figure, and that the true rubber sulfide corresponding to C_5H_8S is not attacked. Even after 2000 hours of acidic extraction the coefficient is still appreciably in excess of the figure of 47 required for this formula. (2) The progressive fall in the ash figure demonstrates the efficiency of this method of analysis, even with vulcanite. The last portions of mineral matter are difficult to remove, but the bulk is extracted early in the operation. However, as previously pointed out,[1] the effect on the coefficient of such a small proportion of

metallic sulfide as may remain is not appreciable and cannot influence the broad interpretation of the previous results.

The Composition of Rubber Sulfide in Ebonite

Experiments were made on the evolution of hydrogen sulfide from ebonite in order to decide whether substitution occurs during vulcanization under these conditions, *i. e.*, with high sulfur content, low temperature of "cure," and in the presence of an ultra-accelerator. The Mixes nos. 1, 2, and 7, as previously detailed, were employed, *viz.:*

	1	2	7
Rubber	100	100	100
Sulfur	35	75	200
Zinc oxide	20	20	20
Zinc diethyldithiocarbamate	5	5	20

The unvulcanized materials were cut into small pieces and placed in sealed flasks connected with U-tubes containing lead acetate solution. The flasks were placed in an electric oven at 70° for 168 hours. No evolution of hydrogen sulfide occurred in this period. The flasks were removed and opened without any specific odor being detected. A further small quantity of unvulcanized stock was introduced and the flasks were replaced in the oven at 100°. After about 16 hours the flasks were re-examined and the black stain of lead sulfide was found in the U-tube of the flask containing compound no. 7. No stain was obtained with compounds nos. 1 and 2. The flasks were replaced in the oven for a short time without any further change occurring. Repetition of the experiment with compound no. 7 confirmed these results, and suitable control tests were also carried out. It is clear, therefore, that hydrogen sulfide is evolved at 100° but not at 70°, which would indicate that substitution occurs only above 70° and then only in the presence of a large excess of sulfur.

Referring again to the paper on "The Nature of Vulcanization, Part IV," it will be seen that at 70° the coefficients of vulcanization obtained with compounds nos. 1 and 2 did not exceed the theoretical value of 47 (no. 7 was not then included). Samples of compound no. 7 were therefore vulcanized at 70° for 168 hours and 336 hours, with the following results:

Time of Vulcn., Hrs.	Combined Sulfur	Ash	Coefficient
168	26.6	14.8	45.4
336	27.1	14.5	46.4

Thus, even with compound no. 7 the coefficient when vulcanizing at 70° approximately reaches but does not exceed the theoretical value, whereas when vulcanized at 100° much higher values were obtained (Part IV, *loc. cit.*).

Since it is only at the higher temperatures that compound no. 7 evolves hydrogen sulfide, it appears that substitution occurs only when figures in excess of the theoretical coefficient of 47.0 are obtained. Somewhere in the range of 70°–100° occurs the critical temperature of the substitution reaction, provided that a sufficiently large excess of sulfur is present. It also follows that if it is desired for theoretical or practical purposes to prepare vulcanite with a coefficient of 47, free from substitution products, the temperature of vulcanizing and proportion of sulfur must be kept low.

References

[1] *J. Soc. Chem. Ind.*, **48**, 55T((1929); Rubber Chemistry & Technology, **2**, 421 (1929).
[2] *Analyst*, **40**, 275 (1915).
[3] *Ber.*, **46**, 1291 (1913).

[From The Physical Review, Vol. 38, No. 9, pages 1790–1791, November 1, 1931.]

Crystalline Rubber Hydrocarbon

E. W. Washburn

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Substantially all of the chemical and physical evidence concerning the nature of rubber is consistent with the chemical formula $(C_5H_8)_x$, and this is the generally

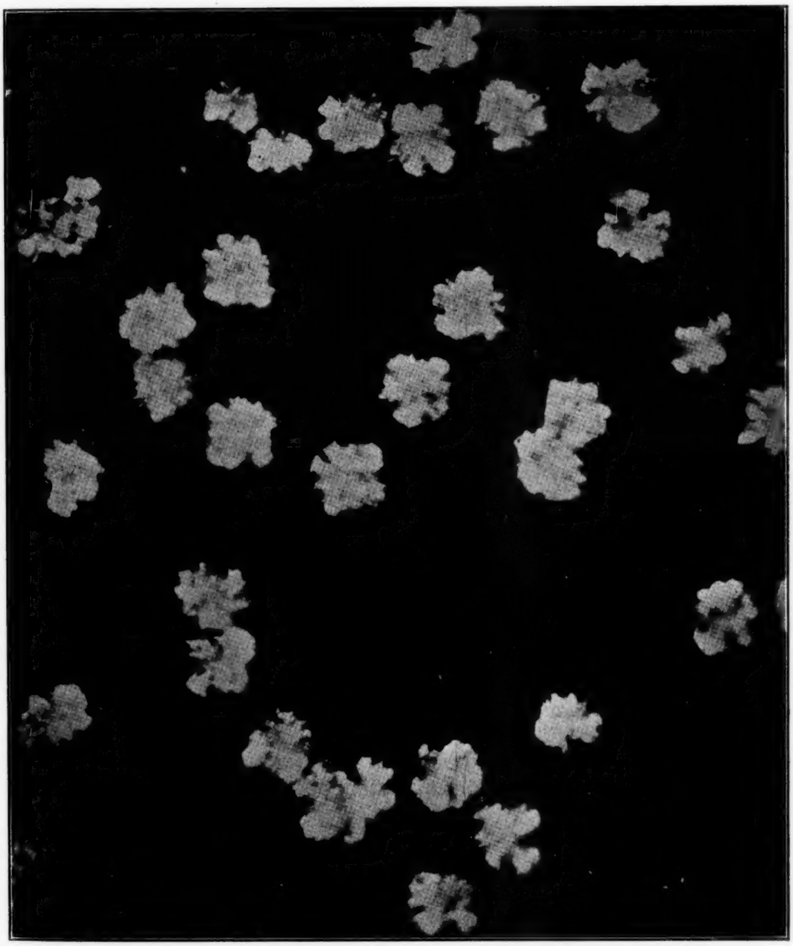

Figure 1—Crystals of Rubber Hydrocarbon Photographed between Crossed Nicols at a Temperature of −55° C. Magnification—200 Diams.

accepted formula for "rubber hydrocarbon." An examination of the evidence discloses, however, that the above formula is not the only one which is consistent with this evidence. The difficulty of establishing beyond question the chemical

composition of "rubber hydrocarbon" has been due largely to the lack of efficient physical methods for fractionating the "hydrocarbon," of proving that the final fractions are one-component systems, and of chemically identifying these fractions. If, as seems not improbable, "rubber hydrocarbon" is a mixture of closely related hydrocarbons, not all of which can be represented by the formula $(C_5H_8)_x$, no single method of fractionation can be relied upon to separate this mixture into its constituents. The only methods heretofore available for this purpose have been those based upon extraction with different liquids and fractional precipitation. One of the most powerful methods for fractionating a mixture of this character is systematic crystallization, and a laboratory technic for applying this method to "rubber hydrocarbon" has recently been developed at this Bureau. The conditions which must be met in order to induce crystallization in such a typically colloidal material as rubber can be predicted. These conditions have been met and are embodied in the following procedure.

The "rubber hydrocarbon," previously purified from all non-hydrocarbon materials, is dissolved to form a dilute solution in a suitable solvent. This solution is cooled to the temperature necessary to induce crystallization, and then is held at the desired temperature until crystallization is completed. The excess solution can then be removed and the crystals dried *in vacuo* for examination.

The accompanying photograph illustrates one type of crystal clusters which are obtained in this way. These crystals were grown at $-55°$ C. from a 0.05 per cent solution of the hydrocarbon in pure dry ether.

The Bureau is now engaged in a determination of the melting point of these crystals, which point lies somewhere between $-35°$ and $0°$ C. The melted crystals are typically rubber-like in nature, and a preliminary combustion analysis indicates a hydrogen-carbon atomic ratio close to 8:5, thus proving beyond any question that the crystals are rubber crystals. It is planned to carry out a systematic fractionation of "rubber hydrocarbon" by repeated crystallizations and to make accurate combustion analyses and molecular weight determinations of the final fractions.

This investigation has been carried out in the Section of Organic Chemistry of this Division under the direction of C. E. Waters. The purification of the "rubber hydrocarbon" and the growing of the crystals were conducted by W. H. Smith, and the combustion analyses were made by H. J. Wing. The photomicrographic technic offered great difficulties, since the crystals had to be photographed in the solution at a temperature of $-55°$ C. The development of this technic was started by F. W. Ashton and brought to successful completion by Charles P. Saylor.

In addition to the crystallization technic described above, it has also been found possible to distill the "rubber hydrocarbon," but fractionation by this procedure is very slow and of value only for confirmation purposes.

[Translated from Comptes Rendus, Volume 193, pages 852–854, 1931.]

The Degradation of Rubber Solutions of Different Concentrations

P. Bary and E. Fleurent

Xylene solutions of rubber of the smoked plantation crepe type were placed in an atmosphere of nitrogen and maintained at a nearly constant temperature of 95° C. Solutions of five different concentrations were employed, namely, 5.12, 3.94, 2.88, 1.98, and 0.99 per cent, and measurements of the viscosity were made as before by the flow through a tube with an inside diameter of about 1 mm.

In curves of the relative viscosity as a function of the time, the hyperbolic law already described (*Comptes rendus* **192,** 946 (1931); RUBBER CHEMISTRY & TECHNOLOGY, **4,** 505 (1931)) was again found to be true, but only for concentrations of 1.98 and 0.99%. With more concentrated solutions the curve presents a characteristic point, and can be separated into two distinct periods:

(*a*) A period of disaggregation of the rubber swollen to the state of jelly in suspension in the xylene. The greater the concentration the more prolonged is this period (*e. g.*, 320 hours for the 5.12 per cent solution and 110 hours for the 2.88 per cent solution).

(*b*) A period of molecular degradation following that just described, during which the viscosity approaches more and more that of the solvent, while following the hyperbolic law observed previously.

Moreover, there exists for xylene a temperature above which there is pyrolysis of the rubber. As we have remarked, in the experiment at 140° this pyrolysis was manifest by a brown coloration of the solution, accompanied by a characteristic odor. These phenomena do not take place at 95° C. Pyrogenation in xylene accordingly commences between these two temperatures.

The higher the concentration, the greater are the viscosity and the time of heating values which are represented by the characteristic points of the viscosity curves of the heated solutions. These points cannot therefore be attributed to an anomaly, for in such a case the anomaly would disappear at a certain definite value of one or the other of the two factors. It therefore seems probable that the hyperbolic law does not begin to correctly represent the degradation, no matter what the concentration, until the molecules have become sufficiently small to reach a state of independence of one another which they did not possess before.

In this second period the viscosity can be represented by the formula already ndicated:

$$\eta - 1 = \frac{A}{t + \theta}$$

The following are the values of the parameters for three of the solutions which were heated for some time:

	A	θ
5.12% solution	3658	−181
2.88% solution	1401	− 47.6
0.99% solution	92.9	− 27.7

The heating at 95° of the three solutions was carried on for a total of 872 hours. However, the origin of the hyperbolic curve is located in each case at a number of hours given by the value of θ considered positive. One is led to the conclusion, in the case, for example, of the 0.99 per cent solution, that the determinations made in the first 27 hours of heating belong to the first period. This shows that the viscosity measurements made in all our experiments after short periods of heating give too low values even for 2 and 1 per cent solutions, and explains the existence of the characteristic point to which we wish to call attention before proceeding further.

[Translated from Revue Générale du Caoutchouc, Vol. IX, No. 78, pages 3–6, January, 1932.]

Micellar and Molecular Solutions of Rubber

Paul Bary

I

The chief interest in studying the degradation of rubber lies in the fact that it makes possible an investigation of the manner in which substances first swell in a liquid before they disperse.

There are two opinions current about the state of rubber in its solutions; one, for several years the most popular, is that rubber consists of micelles in the liquid; the other is that rubber is a molecular dispersion with the molecules in the form of chains which may be very long. This latter hypothesis has been taken up comparatively recently by Staudinger, and is supported by a large number of experiments.

In the investigation being carried out by the author and E. Fleurent on the degradation of rubber, of which the preliminary results have already been published, the object has been first of all to determine the law according to which the degradation progresses with time under different conditions of solvent, concentration and temperature.[1]

When one operates with dilute solutions (0.4 to 2%), the law of degradation is easily proved to be proportional to the time, but these solutions have no appreciable rigidity until they are homogeneous, and all the viscosity measurements of the solutions can be made with a single viscosimeter, without waiting for too long a period of flow.

The case is different with solutions of concentrations greater than 2 per cent. A solution of 5 per cent or more, *e. g.*, one containing 50 grams of rubber per liter in xylene, after having stood six weeks *in vacuo* and having been agitated every two or three days, still has a viscosity of 3000 to 4000 times that of xylene alone. To carry out this measurement under the same conditions as for xylene would require an experiment lasting about 50 hours, which renders it practically impossible.

It is necessary to work not only with an outflow tube condenser of larger diameter, but, in addition, to exert an external pressure on the liquid equal to that of one meter of water. The measurement requires only a few minutes and therefore is practicable. Unfortunately a study of the variation of the time of flow as a function of the pressure proves, as was to be expected, that there are important deviations from the theoretical law of the proportionality of the time of flow to the reciprocal of the pressure.

For example, a xylene solution of rubber (smoked crepe) in the ratio of 15 grams rubber per liter (solution 1) after heating to 45° C. for 705 hours gave the following viscosities according to three different measurements.

1. Viscosimeter No. 1 (small diameter) and additional pressure of 1 meter of water.

$$\eta_{20} = 55.6$$

(η_{20} = ratio of time of flow of the solution to that of xylene at 20° C.)

2. Viscosimeter No. 2 (large diameter) with same external pressure.

$$\eta_{20} = 66.5$$

3. Viscosimeter No. 2 with pressure of 166 mm. water.

$$\eta_{20} = 81.8$$

With the same viscosimeter used with different pressures there is a difference of more than 18 per cent in the values obtained with variations in the pressure of flow from 1000 to 166 mm. of water.

The same result is found with different viscosimeters. The constants of each one, having been determined with the pure liquids, no longer apply to solutions of rubber until a somewhat advanced degradation has taken place.

These results therefore confirm the fact that, when viscosity is expressed in terms of the time of flow of rubber solutions, it has a precise meaning only when the degradation has progressed to a certain degree.

II

The reservation which has just been made explains the new results which the author and Fleurent have recently pointed out.[2]

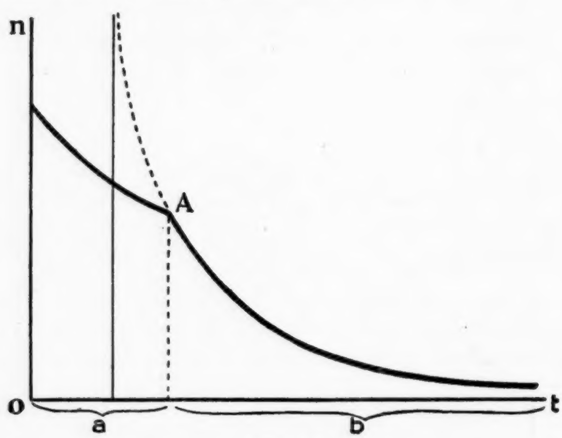

Figure 1

It is seen in fact that the curve which represents the values of the viscosity as a function of the time of heating the solution can be divided into two distinct periods:

(*a*) A period of disaggregation of the rubber swollen to the state of a jelly suspended in the xylene. The greater the concentration the longer is this period (*e. g.*, 320 hours for a 5.12 per cent solution and 110 hours for a 2.88 per cent solution).

(*b*) A period of molecular degradation which follows the preceding one, during which the viscosity of the solution approaches more and more that of the solvent, in accordance with the hyperbolic law observed previously.

Between these two periods there is a characteristic point in the curve which corresponds to a time of heating which increases in duration with increase in the concentration of the solution. It seems probable that the hyperbolic law does not begin to represent the degradation correctly, no matter what the concentration

may be, until the molecules have become sufficiently small to acquire an independence of one another that they did not have previously. Naturally, the more dilute the solution the sooner is this new state reached.

In the first series of experiments all work was done with solutions of 20 grams per liter, that is, very dilute solutions, and although it was confirmed by repeated experiments that the initial measurements of the viscosity deviate a little from the law of the relation of the subsequent values to the time of heating, this deviation was attributed to the fact (which has been referred to elsewhere) that the initial value is uncertain, and it should only be considered valid when the solution is homogeneous.

In the following series of experiments the concentrations varied between 10 and 50 grams of rubber per liter, and the results can be represented in all cases by curves having the form in Fig. 1, which shows a characteristic point, only beyond which is the hyperbolic formula applicable.

III

This new result leads to the conclusion that the structure of the solutions varies with their initial concentration and with their degree of degradation. It will now be shown to what a simple conclusion these results lead, on the hypothesis which it is believed is applicable to all colloidal substances, *viz.*, chemical polymerization.

If it is admitted that the rubber molecule is a polymer of isoprene with the formula $(C_5H_8)_n$ (as is now considered almost certain by nearly every one), and if account is taken of the numerous experiments by Staudinger[3] and his collaborators in which the molecular weight of rubber in solution can be determined from its viscosity measurements, it must be concluded that dilute solutions of rubber are composed of molecules, the molecular weight of which diminishes with time, and the higher the temperature the more rapid is this diminution.

The end point of the degradation is not known. Based on the formula of Staudinger, which shows the relation between molecular weight and viscosity, and the new formula of degradation showing that this viscosity approaches the value of the solvent itself when the degradation is at its maximum, it seems that after this limit is reached the molecule does not have a longitudinal dimension of an order of magnitude greater than that of its transverse diameter. This conclusion leads in turn to the possibility of complete depolymerization, where C_5H_8 is the extreme limit.

In fact, apart from a somewhat advanced degradation but still far from its limit, it becomes impossible to coagulate the solution by acetone in order to recover the rubber it contains. At times a very stable emulsion forms, but the emulsified part does not represent anywhere nearly the total quantity of rubber, the latter having become soluble in acetone.

If the solution is evaporated by a method which permits a determination of the rubber which it contains when the solution is not degraded, there is formed after degradation only a very much smaller quantity of rubber than is to be expected, and the substance obtained is pasty, almost liquid and gluey, like rubber turned to fat.

These results make acceptable the hypothesis of the combination of rubber with solvent, a combination which is the more stable the simpler the molecule of rubber.

IV

From all of these results, particularly those in Section II, the structure of rubber in the solid jelly state, the liquid jelly state, and in solution can be shown schematically as follows:

Fig. 2, considerably enlarged to show the molecules of rubber, represents the jelly form of dispersion. The molecules of rubber are very long and entangled, so as to form a sort of felt, in which the spaces between the fibers are filled with the solvent. It is a case of a solution of the liquid in the rubber. The whole system keeps its solid form as long as the swelling is so slight that the molecules of rubber form an entanglement, which gives rigidity to the system.

If the swelling is increased, breaks take place in the jelly in certain places. The molecules of rubber become shorter and some disperse in the liquid, but the grains of the jelly still remain, giving to the viscous solution a mixture of swollen micelles of the solvent dispersed in a true solution of rubber (Fig. 3). Finally, Fig. 4, representing a greater dilution, shows more advanced degradation, and there are only relatively short molecules dispersed in the liquid mass. This is a true solution of a compound with catenary molecules.

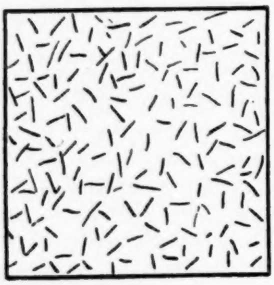

Figure 2—Solid Jelly Solution

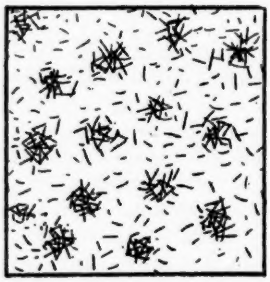

Figure 3—Micellar Solution

Figure 4—True Solution

The intermediate state of Fig. 3 is not a transitory and unusual state; it corresponds to a solution with a concentration of 20 to 30 grams or more of rubber per liter, and it persists for months at ordinary temperature. It disappears more quickly on agitation, stirring, or heating.

This state can easily be verified by slowly pouring the solution into thin layers. It is then seen that the surface is not smooth, and that the liquid resembles tapioca bouillon. This is evident with the naked eye as long as the micelles are sufficiently large, but it persists for a long time after it becomes invisible. The dimensions of the micelles can therefore be very small, and they may be very numerous.

It appears certain that micellar solutions of rubber exist as well as molecular

solutions. It also appears certain that the opinion of Staudinger, that this type of colloidal solution is not applicable to rubber, does not take into account the very frequent form which is intermediate between the jelly (true solid solution) and the homogeneous liquid solution.

V

In the experiments to bring about changes in the rubber, it is impossible to work with the solution without its coming in contact with air at some time. Agitation during solution, dilution of the mother solution at different degrees, putting into sealed vacuum tubes, and measuring the relation between the viscosity and the degradation, are operations, sometimes lengthy, during which the rubber in solution is in contact with atmospheric oxygen.

Because of the sensitivity of rubber to absorption of oxygen, as shown by numerous experiments on mixing this substance in the presence of air and inert gas, especially the recent experiments of Cotton,[4] it was of importance to know the effect of contact of the solutions with air at ordinary temperature.

On this point only the experiments of Staudinger and Leupold[5] are available. These experiments deal with balata in very dilute tetrahydronaphthalene (tetralin) solutions, and show the very appreciable effect of oxygen on the viscosity of the solution, even at ordinary temperature. These authors have, moreover, shown that the same thing is true of rubber, but without stating in any precise way whether the generalization is true of heated solutions and of those kept at the temperature of the laboratory.

An attempt has been made to study the magnitude of the effects which may result from contact of the solutions with oxygen at ordinary temperature by using a method like that used by Dufraisse and Drisch[6] on vulcanized and unvulcanized solid rubber.

Twenty cubic centimeters of a 5 per cent rubber solution in xylene were placed in contact with a known volume of oxygen at atmospheric pressure, and the apparatus was so constructed that the variation of this volume (reduced to the same pressure and the same temperature) could be measured from time to time.

After eight days the absorption of oxygen by the solution, if any had taken place, was less than 0.1 cubic centimeter, which is the limit of sensitivity of the experiment and a negligible quantity. The viscosity of the solution had not changed.

It may therefore be concluded that contact of a sufficiently concentrated solution with oxygen at ordinary temperature is without influence on the results of the measurements.

With the object of determining the extent of this influence at a higher temperature, two flasks containing a known quantity of the same 5 per cent solution were heated at 95° for 264 hours, one containing nitrogen and the other being in contact with air. The viscosity of the solution before heating was about 3000 times that of xylene. At the end of the experiment the viscosities were as follows:

$$\text{In air} \quad \eta_0 = 7.14$$
$$\text{In oxygen} \quad \eta_0 = 8.63$$

The viscosity therefore diminished more rapidly in air, though the difference is not very great.

The fact that at ordinary temperature oxygen seems to have very little effect on rubber when the latter is in a stable state is not surprising, for it is also evident from the numerous and varied experiments by Dufraisse and Drisch, and it is not conceivable that the samples used for measuring the absorption had changed appreciably between their preparation and the time of the experiment.

In order to bring into agreement facts which seem contradictory from certain points of view, it must be admitted that rubber which is not in a state of change, at least not a rapid one, is practically unchanged by the action of oxygen, but that on the contrary if it undergoes degradation by heat or mechanical means (stirring or grinding) the molecular change, which is manifest by a reduction in the length of the polymers, sets free affinities at the extremities of the newly created molecules and renders the rubber susceptible to combination with atmospheric oxygen.

In all these experiments light was excluded, particularly radiations of short wave length whose effects are very intense and different from those which were desired.

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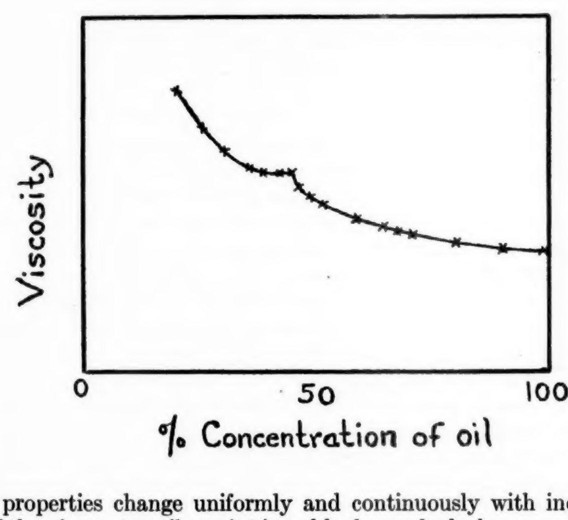
[From Revue Générale du Caoutchouc, Vol. 9, No. 79, page 3, February-March, 1932.]

The Plastic State

G. Antonoff

In the preceding article, Bary has shown a curve of the changes with time in rubber solutions of various concentrations, the interesting feature of which is the angular break which separates the curve into two sections. In a discussion of this paper, attention was called by de Meeus to the fact that it would be interesting to study the physical properties of rubber solutions as a function of the concentration without the complicating effect of aging. This brings up the question whether this curve would also have a similar break. Though data are not available on rubber solutions, it is considered that this is rendered probable by the following facts.

Rubber solutions are true solutions or pseudo-solutions at great dilutions, while they become plastic at high concentrations. Experiments with certain plastic systems have shown a phenomenon which is characterized by the accompanying curve. A study of the physical properties of systems formed of various pigments in suspension in unoxidizable oils, as a function of the concentration, showed that, in



general, the properties change uniformly and continuously with increase in concentration of the pigment until a point is suddenly reached where a very pronounced break in the curve occurs.

Before this point is reached, the system is like that of a fluid, but beyond this point in the region of high concns., the system becomes plastic.

If a thick paste, prepared with a minimum of oil, is diluted progressively with small additions of oil, the curve of the physical properties becomes gradually horizontal before the break in the curve is reached. Beyond this point, the curve descends abruptly, and the system acquires the properties of a fluid.

The horizontal part of the curve seems to indicate the presence of agglomerates, which dissociate into smaller units by dilution. The term "dissociation" is used, not in the sense of chemical combination, but simply with the idea of agglomerated particles with a certain number per unit volume. When the system is diluted, the

particles subdivide into smaller units in such a way that their number per unit volume remains the same.

If the curve for rubber solutions showed the same phenomenon it would certainly indicate the presence of agglomerates. Because of the complex nature of rubber, however, this would indicate nothing definite about the molecular state of the rubber.

[Translated from Helvetica Chimica Acta, Vol. 13, No. 6, pages 1355–1360, December, 1930.]

Isoprene and Rubber

Part 28.[1] The Fractionation and Cracking of Hydrorubber

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The Fractionation of Hydrorubber

According to the investigations of Geiger,[2] treatment of rubber with hydrogen in the presence of nickel at 270° brings about a reduction with simultaneous cracking of the macromolecules of the rubber. The hemi-colloidal hydrorubber thus formed ought not to consist of uniform long molecules, but of a mixture of homologous polymers; because in other similar cases mixtures of homologous polymers were obtained when macromolecular substances are decomposed, *e. g.*, in the acetolytic decomposition of polyoxymethylenes[3] and of cellulose.[4] According to the views of Pummerer, on the other hand, if rubber consists of relatively small molecules, there would be no decomposition by cracking during its reduction, but only a saturation of individual primary valence chains with breaking up of the micellar structure, with formation of a hydrorubber whose molecules are uniformly long. Pummerer and Koch[5] believed that they had obtained such a substance.

To prove whether hydrorubber consists of a mixture of homologous polymers, it was split up into five fractions by fractional precipitation with alcohol from its ethereal solution, and the viscosities of the individual fractions were determined in 0.5 molar carbon tetrachloride solution (Table I).

As a result, it was found that hydrorubber actually consists of a mixture of homologous polymers which are separable by fractionation. The more easily soluble portions give less viscous solutions than the more difficultly soluble parts. This fractional precipitation of hydrorubber leads therefore to a separation into lower and higher molecular products, as is evident by the relation between viscosity and molecular weight. In order to give a rough picture of the molecular weights of the individual fractions, the constant K_c was calculated from the η_r values and it was further assumed that the molecular weight is the same as that of rubber $K_c \times 10^4$.[6] The most difficultly soluble fraction has, according to this calculation, an average molecular weight of about 20,000, therefore as a result of the rapid reduction relatively large fragments of rubber remain intact. Purified rubber itself, which has an average molecular weight of about 70,000[6] on heating to 270° C., as was explained in a preceding article,[7] would decompose into much smaller fragments, into hemi-colloids having a molecular weight of 2000 to 3000.

TABLE I

FRACTIONATION OF RUBBER

Fraction	Solubility	Amount in %	In 0.5 Mol. Soln.	$K_c \frac{\log}{c}$	Molecular Weight, K_{cm} 10^4
Mixture	Medium	100	4.90	1.38	14,000
Fraction I	Regular decrease of ↓	9.1	1.80	0.51	5,000
Fraction II	solubility in ether-	18.5	2.47	0.79	8,000
Fraction III	alcohol mixture	49.1	3.84	1.17	12,000
Fraction IV		10.3	6.46	1.62	16,000
Fraction V		12.9	11.86	2.15	21,000

Distillation and Cracking of Hydrorubber

According to Pummerer and Koch,[8] hydrorubber remains partially undecomposed when distilled in high vacuo. The authors obtained a saturated hydrocarbon $(C_5H_{10})_{10}$ as a distillate, and this result was regarded as proof of the micellar structure of rubber from small base molecules. According to Fritschi,[9] the high molecular hydrorubber is cracked during distillation. The distillate consists of lower molecular decomposition products which are unsaturated. It follows without further question from viscosity determinations of uncracked and cracked hydrorubber that the assumption of Pummerer and Koch that hydrorubber can be distilled without decomposition is incorrect. For example, if a high molecular hydrorubber prepared in the cold is distilled in absolute vacuo, according to the directions of Pummerer and Koch, distillates are obtained which yield very much less viscous solutions than the original material.

$\frac{\eta_{sp}}{c}$ of the hydrorubber prepared in the cold = 6.1[10]

$\frac{\eta_{sp}}{c}$ of the distillate I Fraction = 0.5

$\frac{\eta_{sp}}{c}$ of the distillate II Fraction = 0.5

Cracking a hemi-colloidal hydrorubber prepared at 270° gave the following values:

$\frac{\eta_{sp}}{c}$ of hemi-colloidal hydro-rubber = 3.9

$\frac{\eta_{sp}}{c}$ of the distillate = about 0.3

To this Pummerer can say that hydrorubber distils undecomposed only if he regards such significant differences in the viscosity of solutions of the same concentration as of no account in explaining the constitution, and if he assumes that these differences depend upon a difference in the micellar structure. Since, however, it has been proved that differences in the viscosity of solutions of the same concentration of homologous polymeric compounds depend[11] upon differences in the length of the molecule, it follows from the above measurements that in the distillation of hydrorubber an extensive cracking occurs, and furthermore that hydrorubber has a much higher molecular weight than this product of the cracking.

As far as the cleavage of hydrorubber is concerned, as has already been reported previously,[12] it is much more difficult than that of rubber, since the unsaturated chain of the latter is particularly unstable because of the double bonds. The cleavage of stable hydrorubber chains may possibly take place in such a way that there is a migration of the tertiary hydrogen atom, as can be shown thus:

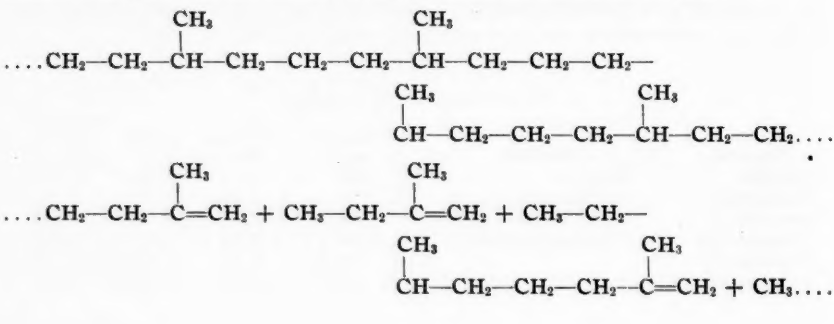

TABLE II

DISTILLATION OF HYDRORUBBER IN HIGH VACUO

Fractions	Molecular Weight According to Rast	Molecular Weight by Titration	Number Isoprene[20] per Δ	η_r in 0.5 Mol. CCl_4 Solution	$\frac{\eta_{sp}}{c}$	K_m from Molecular Weight (I)	K_m from Molecular Weight (II)
I. Boiling point below 100° at 0.1 mm.	..	180	2.6	1.0			
II. Boiling point from 100°–150° at 0.1 mm.	310	310	4.4	1.02[21]	0.04	1.3×10^{-4}	1.3×10^{-4}
III. Boiling point from 150°–200° at 0.1 mm.	400	370	5.3	1.06	0.12	3.0×10^{-4}	3.2×10^{-4}
IV. Boiling point from 250°–265° at 0.1 mm.	440	520	7.5	1.08	0.16	3.6×10^{-4}	3.1×10^{-4}
V. Boiling point above 300° at 0.1 mm.	940°	960	13.7	1.16	0.32	3.4×10^{-4}	3.3×10^{-4}
Undistilled hydrorubber reduced at 270° in the swollen state	Molecular weight calculated from $\frac{\eta_{sp}}{c}$ 16,000		..	6.01	4.9[22]		

The lowest molecular cleavage fragment is therefore a methylethylethylene which was detected in small quantity by Huber.[13] The cleavage of the hydrorubber chains takes place similarly; therefore a mixture of homologous ethylene derivatives should be found. From the dissimilar migration of the hydrogen atoms, naturally saturated cleavage fragments might result, together with those having two double bonds at the end of the molecule. Since, however, a mixture of such products cannot be separated, it will be possible here, too, to prove by analysis an average of one double bond per molecule. This result was also obtained. The distillation product of hydrorubber is unsaturated; contrary to Pummerer and Koch we were not able to observe a saturated distillation product.[14] If the dis-

TABLE III

DETERMINATION OF THE DOUBLE BONDS IN DISTILLED HYDRORUBBER BY TITRATION WITH IODINE CHLORIDE ACCORDING TO THE METHOD OF McILHINEY[23]

Fractions	Substance in G.	No. of G. of Iodine Used	No. of Cc. of 0.1 N Thiosulfate Solution	% Double Bonds	Number of Isoprenes per Double Bond
I. Boiling point below 100° at 0.1 mm.	0.0605	0.0857	6.75	37.9	2.6
II. Boiling point from 100°–150° at 0.1 mm.	0.1024	0.0867	6.83	22.7	4.4
III. Boiling point between 150° and 200° at 0.1 mm.	0.1060	0.0744	5.86	18.8	5.3
IV. Boiling point from 250°–265° at 0.1 mm.	0.1002	0.0500	3.92	13.4	7.5
V. Boiling point above 300° at 0.1 mm.	0.1012	0.0275	2.17	7.3	13.7
Undistilled hydrorubber	0.1010	....	..	..	..

tillate is fractionated and the molecular weight of the separate fractions determined according to the method of Rast, approximately the same values are obtained as when the molecular weight is determined by titration with bromine, on the basis that one double bond is present for every molecule. By carrying out the fractionation in a particularly careful manner, it was possible to obtain as the highest molecular cleavage product a hydrocarbon which contained twelve isoprene residues in its molecule, whereas the highest molecular cleavage product obtained by Fritschi had ten isoprene residues in the chain. Since this product gives solutions of very low viscosity, the hydrorubber whose solutions are very highly viscous must have a much higher molecular weight.[15]

If the cleavage products represent a homologous series of ethylene hydrocarbons, then here, too, there should be a relation between the viscosity and molecular length, as with the paraffins.[16] If the constant K_m is calculated from the $\frac{\eta_{sp}}{c}$ values according to the formula: $K_m = \frac{\eta_{sp}}{cM}$, and using in the calculations the molecular weight found according to the method of Rast, and then those determined by titration values, values are obtained which in the case of the highest three fractions[17] lie between 3.0×10^{-4} and 3.6×10^{-4} per isoprene residue and per C_5H_{10} residue, respectively; the constant has therefore about the same order of magnitude as was found in the series of polyprenes[18] and polypranes.[19]

TABLE IV

MOLECULAR WEIGHT DETERMINATIONS OF THE FRACTIONS IN CAMPHOR ACCORDING TO THE RAST METHOD

Fractions	Solvent in G. Camphor	Substance in G.	Depression Highest	Depression Medium	Depression Lowest	Molecular Weight Lowest	Molecular Weight Medium	Molecular Weight Highest
II. Boiling point from 100°–150° at 0.1 mm.	0.2340	0.0205	11.4	11.2	10.9	307	313	322
III. Boiling point from 150°–200° at 0.1 mm.	0.2042	0.0209	10.4	10.2	9.9	394	400	414
IV. Boiling point from 250°–265° at 0.1 mm.	0.2084	0.0274	12.2	11.9	11.8	431	442	446
V. Boiling point above 300° at 0.1 mm.	0.2682	0.0262	4.4	4.2	3.9	888	930	1002

References

[1] See Part 27, RUBBER CHEMISTRY & TECHNOLOGY, Vol. IV, 543 (Oct., 1931).

[2] *Thesis*, Geiger, Zürich, **1926**, also preceding communication.

[3] Staudinger and Lüthy, *Helvetica Chim. Acta*, **8**, 41 (1925); Staudinger and Signer, *Ann.*, **474**, 172 (1929).

[4] Staudinger and Freudenberger, *Ber.*, **63**, 2331 (1930).

[5] Pummerer and Koch, *Ann.*, **438**, 303 (1924).

[6] Staudinger, *Ber.*, **63**, 921 (1930); *Kautschuk*, **6**, 153 (1930); also preceding communication.

[7] See preceding communication; also Staudinger and Geiger, *Helvetica Chim. Acta*, **9**, 549 (1926).

[8] *Ann.*, **438**, 303 (1924); also "Handbuch der Kautschukwissenschaften," page 253.

[9] Staudinger and Fritschi, *Helvetica Chim. Acta*, **5**, 785 (1922).

[10] The viscosity was determined in such a dilute tetralin solution that η_{sp} = 0.3–0.5; from which was obtained the value $\frac{\eta_{sp}}{c}$, see following communication.

[11] Staudinger, *Ber.*, **59**, 3031 (1926); *Kolloid-Z.*, **51**, 71 (1930).

[12] Staudinger, *Ber.*, **57**, 1205 (1924).

[13] Huber, *Thesis*, Zürich, **1926**.

[14] Only 0.6 g. of a hydrorubber in solution (prepared according to Pummerer and Koch) was distilled, obtaining the results mentioned above. On a larger scale only a reduced hydrorubber in the swollen state at 270°, having a molecular weight of 16,000, was cracked. Attention should be called to the difficult purification of the hydrorubber from the catalyst, especially in the reduction with platinum. With the use of colloidally divided catalyst, extensive decompositions might naturally occur.

[15] Staudinger, *Kautschuk*, **4,** 94 (1929).

[16] Staudinger and Nodzu, *Ber.*, **63,** 721 (1930).

[17] The great deviation with low molecular substances may be due to inaccurate measurements.

[18] Staudinger and Bondy, *Ber.*, **63,** 734 (1930).

[19] Staudinger and Nodzu, preceding communication.

[20] Isoprene residue C_5H_{10}.

[21] In this solution of very low viscosity η_r is difficult to determine, and the deviations in the constants may be attributed perhaps to this difficulty.

[22] Calculated from 0.1-molar solution; $\eta_{sp} = 0.49$.

[23] *J. Am. Chem. Soc.*, **21,** 1087 (1899).

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Isoprene and Rubber

Part 29.[1] High Molecular Hydrorubbers

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The molecular concept in organic chemistry is based upon the fact that the molecules, whose existence is proved by vapor density determinations, enter into chemical reactions as the smallest particles. If now it is assumed that organic molecular colloids like rubber are dissolved in dilute solution in molecular form then it must be proved that in the chemical transposition of macromolecules as well no change in the size of the macromolecules occurs. In the case of hemi-colloids, therefore for molecular colloids with an average molecular weight of 1000 to 10,000, this has been proved[2] by the reduction of polyindenes,[3] especially of polysterenes,[4] to hydroproducts with the same average molecular weight, and also by the fact that cyclorubbers[5] do not change their molecular weight upon autoöxidation. The molecular weights of hemi-colloidal hydrocarbons are therefore invariable.

This is much more difficult to prove in the case of rubber, although there are many more ways in which unsaturated rubber can be transposed than the stable polysterenes, polyindenes, and polycyclorubbers. In most of the reactions with rubber, as in its action with nitrosobenzene, oxidizing agents, hydrogen halides, and halogens, an extensive decomposition takes place as a result of the instability of the molecule, which is referred to in another work.[6] Therefore derivatives of rubber are not formed, but derivatives of hemi-colloidal decomposition products. The catalytic reduction of rubber in the cold appears to be the most suitable process of making it react without changing its molecular size in order to prove that in a chemical transposition its molecular weight remains the same.

A rubber purified according to the method of Pummerer and Koch was used for the first experiment. This was very easily soluble in ether and had a relatively small average molecular weight of about 45,000 according to viscosity measurements. The limiting concentration of such a rubber, *i. e.*, the concentration at which a sol solution passes over to a gel solution, is reached in a solution of approximately one per cent. Solutions below one per cent are accordingly soluble solutions with freely moving molecules. Platinum oxide, prepared according to the method of Adams and Shriner,[7] which is especially active, was used as a catalyst. The hydrorubber obtained had a molecular weight of about 30,000. Therefore in the reduction a relatively insignificant decomposition took place.

The reduction of rubber in the cold with platinum or platinum oxide as catalyst very frequently fails. Abnormal hydrogenation occurs,[8] *i. e.*, cyclicization and hydrogenation.[9] It still remains to be proved experimentally whether these cyclicizations result if reduction takes place in the range of a gel solution.[10]

It is much easier to obtain relatively high molecular hydrorubber by reducing rubber with a specially active nickel catalyst in hexahydrotoluene solution at 150°–200° in a rotary autoclave with high hydrogen pressure. In the presence of large amounts of catalyst, the reduction can be easily controlled under experimental conditions, so that hydrogenation to the stable hydrorubber takes place quickly and the decomposition is not deep seated. From a rubber of average molecular

weight of about 70,000, a hydrorubber of average molecular weight of 30,000 was obtained.

Although the problem of transposing the rubber molecule in such a way that its magnitude remains the same is not yet solved, reduction gives very high molecular hydrogenation products. These results once more prove the concept that rubber is very high molecular, and they show also that its molecular weight must lie above 30,000. A molecular weight of about 5000, as is assumed by a few investigators,[11] is out of the question for rubber, according to these experiments.[12] With exact knowledge of the extraordinary ease with which the rubber molecule can be modified,[13] experiments on the reduction of rubber at ordinary temperature should be continued and the reduction so carried out that no decomposition occurs in the molecule, *i. e.*, that from a eucolloidal rubber of a molecular weight of about 70,000 a hydrorubber of the same molecular weight is obtained. Such a high molecular hydrorubber would be of great interest in judging the physical properties of rubber, especially its elasticity, because the hydrorubber of a molecular weight of 30,000 already has feebly elastic properties.

Preparation of High Molecular Hydrorubber

If one reduces rubber in solution to high molecular hydrorubber it is found that it is extremely difficult to remove the catalyst from this hydrorubber. The preparation of pure products is thus very difficult, in contrast to the hemi-colloidal hydrorubbers prepared at 270°, which are easily separated from the catalyst by repeated precipitation or centrifuging. The different behavior is due to the fact that about 2.5% solutions of high molecular hydrorubber yield gel solutions, whereas solutions of similar concentration from low molecular hydrorubbers are sol solutions. The limiting concentration of a hydrorubber of a molecular weight of 30,000, *i. e.*, that concentration at which the sphere of action of the molecules is as great as the space at their disposal, is reached at 1.4% and, in the case of a hemi-colloidal hydrorubber of a molecular weight of 3400, at about 10%. The catalyst is surrounded, as it were, by the long molecules of high molecular hydrorubber; the high molecular hydrorubber is a better "protective colloid" for the colloid particles of the metal than is the low molecular rubber.[14] We succeeded in purifying a high molecular hydrorubber from the catalyst by agitation in a very dilute—at the highest 1%—solution with magnesium oxide, in which case the catalyst was adsorbed.[15]

Preparation of High Molecular Hydrorubber with Platinum Oxide in the Cold

An ether-soluble rubber, purified according to Pummerer's method, was used for the reduction. According to viscosity determinations it had a molecular weight of about 45,000. The limiting concentration of the solution is therefore reached at about 1%. For the reduction a 0.1% solution in purified hexahydrotoluene, *i. e.*, a sol solution, was used. One hundred cubic centimeters of this solution were agitated with six grams of platinum oxide, which was added in portions of one gram every six hours, and this addition was continued until the solution was completely saturated to bromine and tetranitromethane. To separate the colloidally dispersed platinum, the mixture after being greatly diluted was shaken several times with magnesium oxide, but the catalyst could not be completely separated in this way. The hydrorubber obtained after evaporation was rather dark colored. To purify it, it was dissolved in hexahydrotoluene and precipitated with methyl alcohol; then dried in high vacuo to constant weight for a week at about 50°.

5.749 mg. substance gave 18.07 mg. CO_2 and 17.13 mg. H_2O
5.322 mg. substance gave 16.70 mg. CO_2 and 6.72 mg. H_2O
$(C_5H_{10})_x$ calculated C 85.62 H 14.38%
found C 85.72; 85.58 H 13.88; 14.13%.

RELATIVE VISCOSITY η_r IN 0.2-MOLAR TETRALIN SOLUTION IN THE UBBELOHDE VISCOSIMETER OF HYDRORUBBER AND OF THE RUBBER USED IN THE EVAPORATION

	20°	40°	60°	Molecular Weight[16] $= K_eK_{cm}$
Hydrorubber	4.22	4.20	4.25	31,000
Rubber	7.75	7.50	7.28	45,000

Since the viscosity of hydrorubber is the same at different temperatures, molecules and not micelles are dissolved.[17]

Preparation of High Molecular Hydrorubber with Nickel at an Elevated Temperature

A rubber purified according to the method of Pummerer, which was difficultly soluble in ether, was used. It had a very high average molecular weight (70,000). The limiting concentration of solutions of this rubber was at 0.4%. 0.06 per cent of the solution was reduced, and 30 cc. of the latter were put in a glass receptacle in the Fierz rotary autoclave with 1.5 g. of active nickel catalyst of Hückel and hydrogenated at about 100 atm. pressure of hydrogen at 180°–200°. After two hours the solution was completely saturated to bromine and tetranitromethane. The nickel catalyst could be more easily removed than the platinum, likewise by agitation of the diluted hexahydrotoluene solution with magnesium oxide. For further purification the diluted hexahydrotoluene solution was poured into methyl alcohol at 0° and the process repeated. This product, too, had to be dried about two weeks in high vacuo to constant weight.

5.825 mg. substance gave 18.30 mg. CO_2 and 7.32 mg. H_2O
4.141 mg. substance gave 13.05 mg. CO_2 and 5.38 mg. H_2O
$(C_5H_{10})_x$ calculated C 85.62 H 14.38%
found C 85.68; 85.94 H 14.06; 14.54%.

Viscosity Determinations

The hydrorubber prepared according to the above method is the highest molecular product obtained until now. Viscosity measurements of this product are of interest because they show the great difference between rubber and hydrorubber. Viscosity measurements of rubber solutions gave (as will be shown in a later work[18]) widely varying values On agitation, on standing in air, chiefly however on heating to 60°–100°, the viscosity of a rubber solution diminishes, and this does not depend, as was believed earlier, upon a decomposition of micelles or a change in the structure of the liquid, but it is to be attributed solely to the fact that the macromolecules of rubber are extremely sensitive[19] as a result of the double bonds and the consequent instability of the carbon bonds. This follows from the fact that solutions of high molecular hydrocarbons with saturated chains, which have the same colloidal properties as rubber, are completely stable.

Solutions of hemi-colloidal hydrorubber are not changed on agitation, on heating, nor by air. They behave therefore like polysterene solutions.[20] As a result of their stability, solutions of these saturated high molecular hydrocarbons are much more suited to viscosity investigations than those of rubber, which have until now been studied almost exclusively.

That hydrorubber is dissolved molecularly was proved by viscosity measurements at different temperatures. In dilute solutions (0.1-molar and even more dilute) the specific viscosity did not change when the solution was heated from 20°–60°.

The same result was found in the case of polysterenes,[21] whereas heating rubber solutions caused the specific viscosity to drop, since here a decomposition occurred as a result of the sensitivity of the molecules.[22]

In a 0.5-molar hydrorubber solution on the contrary, η_{sp} at 60° is less than at 20°. Here there is a change in the size of the colloid particles which can be attributed to association in the concentrated solution. The same thing was also observed in the case of polystyrenes.

η_{sp} OF HYDRORUBBER IN TETRALIN SOLUTION AT DIFFERENT TEMPERATURES

Molarity	20°	60°	
0.1	1.21	1.22	No association
0.25	4.85	4.41	....
0.5	14.35	11.53	Strong association

The solutions of the highest molecular hydrorubber show only very small deviations from the Hagen-Poiseuille law. According to studies of homologous polymeric polystyrenes and polyprenes, these deviations occur only with much higher molecular compounds, *i. e.*, only with those of a molecular weight of over 50,000. These deviations are very large only in the case of the highest molecular compounds, *i. e.*, polystyrenes and rubbers of a molecular weight of 100,000 to 200,000. Therefore, in the calculation of the molecular weight from viscosity measurements these deviations may be disregarded because of their insignificance with hydrorubbers.

η_{sp}. OF HYDRORUBBER IN TETRALIN SOLUTION AT DIFFERENT PRESSURES IN THE UBBELOHDE VISCOMETER

Molarity	10 Cm.	30 Cm.	60 Cm.
0.5	14.35	13.95	13.60
0.25	4.85	4.87	4.87

In dilute solutions the specific viscosity increases in proportion to the concentration. $\frac{\eta_{sp}}{c}$ is approximately constant. In concentrated solutions, on the other hand, strong deviations occur, because then gel solutions are present and association results ultimately. With a molecular weight of hydrorubber of about 30,000 to 35,000, the limiting concentration is at approximately 0.15 molar solution. According to earlier experiments the viscosity increases very suddenly in the range of gel solution. This is also the case here. The following table shows the great increase in viscosity between a 0.1 and a 0.25 molar solution, as can be seen from the deviation from the calculated η_{sp} value.[23]

VISCOSITY OF HYDRORUBBER IN TETRALIN SOLUTION AT 20°

Molarity	η_r	$\frac{\eta_{sp}}{c}$	Deviation in % of $\frac{\eta_{sp}}{c}$ from Original Value	$K_c = \log \frac{\eta_r}{c}$
0.01	1.09	9.0	...	3.7
0.025	1.24	9.6	6.5	3.7
0.05	1.50	10.0	11	3.5
0.1	2.16	11.6	29	3.3
0.25	5.85	19.4	116	3.1
0.5	15.3	28.6	220	2.4

From the average of the lowest three $\frac{\eta_{sp}}{c}$ values a molecular weight $M = \frac{\eta_{sp}}{cK_m}$ about 32,000 was calculated by means of $K_m = 3 \times 10^{-4}$.[24] From K_c, M = about 35,000, according to the formula $M = K_c K_{cm}$, where $K_{cm} = 10^4$, as was assumed in the polyprene series.

References

[1] See Part 28, preceding.

[2] Staudinger, *Ber.*, **59**, 3033 (1926); Staudinger, Frey, and Starck, *Ibid.*, **60**, 1782 (1927).

[3] Staudinger, Johner, Schiemann, and Wiedersheim, *Helvetica Chim. Acta*, **12**, 962 (1929).

[4] Staudinger and Wiedersheim, *Ber.*, **62**, 2406 (1929).

[5] Staudinger and Bondy, *Ibid.*, **62**, 2411 (1929).

[6] Staudinger and Joseph, *Ibid.*, **63**, 2888 (1930).

[7] *J. Am. Chem. Soc.*, **45**, 2171 (1923).

[8] For abnormal hydrogenation, see Pummerer and Koch, *Ann.*, **438**, 303 (1924).

[9] See Part 25.

[10] There is the possibility that cyclicization during reduction in the cold takes place especially easily if the molecules do not move freely. With a very high molecular rubber, if this view is correct, the reduction must be carried out in much more dilute solution in order to still work within the range of sol solution, as with a low molecular rubber.

[11] Pummerer, "Handbuch der Kautschukwissenschaften," page 267, Verlag, Hirzel; Meyer and Mark, *Ber.*, **61**, 1939 (1928).

[12] This assumption has already been disproved by observations that hydrocarbons of a molecular weight of 5000, which are known in greater number, have hemi-colloidal properties; see Staudinger, *Ber.*, **59**, 3031 (1926). This difference between hemi-colloidal and eucolloidal hydrocarbons is not considered in the corresponding work. See Note 5 above.

[13] Unpublished experiments by Bondy.

[14] The relation between molecular length of high molecular substances and the activity of a substance as a protective colloid will be considered elsewhere.

[15] Pummerer and Koch, *Ann.*, **438**, 306 (1924) suggest alumina, animal black and kieselguhr for the clarification of hydrorubber.

[16] $K_c = \frac{\log \eta_r}{c}$; $K_{cm} = 10^4$.

[17] See following section.

[18] Unpublished experiments by Bondy.

[19] Staudinger and Rheiner, *Helvetica Chim. Acta*, **7**, 25 (1924).

[20] Staudinger and Frey, *Ber.*, **62**, 2909 (1929); Staudinger and Heuer, *Ibid.*, **62**, 2933 (1929).

[21] Staudinger and Heuer, *Ibid.*, **62**, 2933 (1929).

[22] Unpublished experiments by Bondy; see also Staudinger and Leupold, *Ibid.*, **63**, 730 (1930), Viscosity studies on balata.

[23] See analogous studies on rubber by Staudinger, *Ibid.*, **63**, 933 (1930).

[24] See part 27 by Staudinger and Nodzu.

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Isoprene and Rubber

Part 30[1]. Hydromethylrubber

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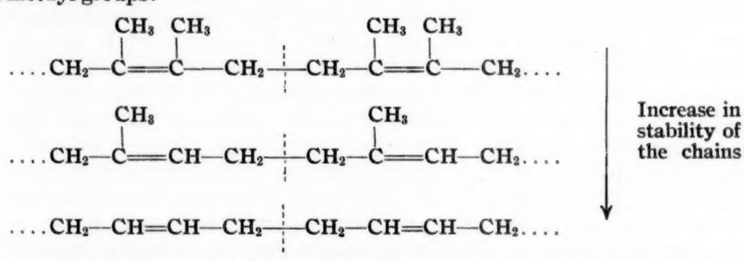
When rubber is reduced at 270° under high pressure, a hemi-colloidal hydrorubber is obtained, and it was proved by Geiger[3] and Huber[4] that the product has a higher molecular weight and is less cyclicized if a good catalyst is used in large quantity (for example, active nickel produced by the method of Kelber[5]), while according to the original experiments of Fritschi, who carried out the hydrogenation in the presence of very little platinum, a more degraded and somewhat cyclicized hydrorubber is obtained. The saturated hydrorubber is much more stable than the unsaturated rubber[6] since the loosening action of the double bonds is lacking. A hydrorubber of the average molecular weight of 10,000 is still relatively stable at 270°, while a hemi-colloidal rubber with this molecular weight will be cracked to still smaller fragments at this temperature, and these fragments are then changed by cyclicization.[7]

This behavior can be clearly seen in methylrubber.[8] The following reduction proves that it is even more easily decomposed than rubber itself. With nickel as catalyst, Geiger obtained from methylrubber by reduction at 270° and 100 atmospheres a hemi-colloidal hydromethylrubber which had an average molecular weight of 1600 and therefore had a degree of polymerization of about 20. If rubber is reduced under the same conditions a higher molecular product is obtained with an average molecular weight of 3000 to 10,000. Judged by reduction experiments, the chain of butadiene rubber is still more stable, since the hydrobutadiene rubber prepared under the same conditions had the highest average molecular weight.[9] The cleavage of the chains,[10] as in the following formula,[11] is therefore favored by the methyl groups:



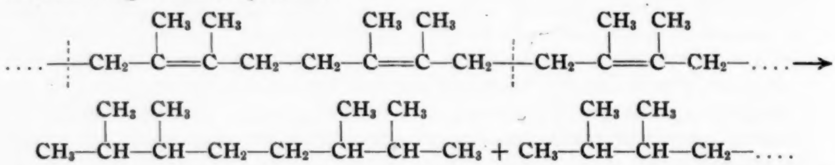
This agrees with the experiments of von Braun,[12] where the stability of the allyl groups is diminished[13] by methyl substitution.

Chemically the hydromethyl rubber behaves like hydrorubber. Both are stable like a paraffin hydrocarbon. From the physical point of view there are slight differences, which correspond to the differences in the length of the chains of both products. Thus, hydromethylrubber is somewhat less viscous than hydrorubber. It yields a very tough colorless sirup; the viscosity of the solution corresponds to the lower average degree of polymerization than that of hydrorubber and especially of hydrobutadiene rubber.

A still greater decomposition of hydromethyl rubber occurs when it is reduced at

270° in the presence of a little platinum, according to the method of Fritschi. A hydrorubber, obtained from rubber according to this method, is more strongly degraded than that obtained with nickel as catalyst.[14] Here such highly degraded products are formed that they may be distilled undecomposed. A dimeric product is the lowest member obtained with rubber; such a reduction with accompanying extensive cracking occurs only at far higher temperatures, *viz.*, 350°.

The following series of methylated paraffins would be expected as reduction products: C_6H_{14}, $C_{12}H_{26}$, $C_{18}H_{38}$, etc., and the hydrocarbon $C_{12}H_{26}$ should yield the following tetramethyloctane:



As already stated above, the cleavage of the long chains takes place between the C—C bonds, which have been loosened by the proximity of the double bonds. During the cracking and simultaneous reduction, the ends of the chains should be first saturated with hydrogen, and then a further reduction of the double bonds should result so that paraffins would be formed. However, according to analysis, these hydrocarbons possess a greater carbon content and a smaller hydrogen content. The completely saturated hydrocarbons obtained have the composition:

$$C_{12}H_{24} \qquad C_{18}H_{34} \qquad C_{24}H_{46}$$

In no case therefore is a paraffin formed, but instead reduction is accompanied by cyclicization. It cannot be determined even today which is the primary reaction, the cyclicization or the reduction, and therefore whether after the cleavage of the carbon chain the free end groups are saturated only by cyclicization or by additions of hydrogen. These and similar hydrogenation cleavages will be further studied, however, because they will give an insight into the cracking of long chains.

The highest molecular product which was obtained with platinum as catalyst had a degree of polymerization of twelve. Like hydrorubbers, but unlike the lower members, it is insoluble in alcohol and acetone. The solubility in alcohol and acetone diminishes very rapidly in this series of homologous hydrocarbons.

In order to obtain higher molecular representatives of hydromethyl rubber, studies were made to reduce the latter at 100°–150° under high hydrogen pressure, in the presence of cyclohexane. The reduction products obtained were still unsaturated, and therefore were not studied further. Their purification should be taken up again, for during hydrogenation there occurs solution of the methyl rubber, which had previously only been swollen. It is to be hoped that in this way viscosity measurements will give an insight into the molecular size of these hydrogenation products and also of methylrubber.[15]

Experimental Part

The methylrubber at our disposal was entirely insoluble in ether and cyclohexane; it swelled in benzene, chloroform, and carbon tetrachloride without going into solution completely. It was purified by swelling in benzene, precipitation with alcohol, and washing with acetone.

Titration with Bromine

0.300 g. methylrubber dissolved in 20 cc. CS_2 required 18.0–18.5 cc. Br_2 solution
C_6H_{10} calculated 18.3 cc. 0.2-*N* Br_2 solution

Hydrogenations with Platinum in Solution

The platinum black used in the hydrogenations was prepared according to the method of Feulgen.[16]

I. 0.5 g. Methylrubber swollen in 80 cc. of purified hexahydrotoluene was heated with 0.5 g. platinum black at a hydrogen pressure of 50 atm. in the Fierz rotary autoclave[17] for 24 hours at 100°.

II. 0.5 g. Methylrubber in 50 cc. hexahydrotoluene, 0.5 g. platinum; heated at 70 atm. 65 hours to 140–155°.

III. 0.5 g. Methylrubber in 50 cc. hexahydrotoluene, 0.5 g. platinum; heated to 180° at 70 atm. 20 hours.

In none of the three experiments did complete hydrogenation take place; instead the products were highly unsaturated and reacted with concentrated nitric acid upon heating, although somewhat less than ordinary methylrubber. The rubber was completely dissolved by the long heating in the autoclave, indicating that depolymerization, perhaps partial hydrogenation, had taken place.

Hydrogenations with Platinum at 270° in the Absence of Solvent

The hydrogenations were carried out as with natural rubber. Methylrubber (40 g.) was dusted with platinum black (1 g.) and heated to 270°–280° in the rotary autoclave at 80°–100 atm. hydrogen pressure. The viscous, liquid reduction product, which was saturated to bromine, had a violet fluorescence and was very stable to concentrated nitric acid, even upon heating. The hydrogenation product separated from the unreduced methylrubber, which is dissolved by warm concentrated nitric acid under violent reaction and the evolution of nitric oxide.

The reaction product was dissolved in ether and precipitated with alcohol. The lower portion of the reaction products which could be distilled remained in the ether-alcohol mixture; the higher molecular part precipitated as a thick yellow liquid. The evaporated ether-alcohol solution was extracted with acetone, the acetone evaporated, and the liquid residue distilled in high vacuo. Decomposition did not occur until the very end of the distillation.

Fraction I boiled 50°–70° at 0.12 mm., about 1.3 cc.
Fraction II boiled 70°–120° at 0.12 mm., about 3.0 cc.
Fraction III boiled 120°–130° at 0.12 mm., about 0.7 cc.

Fraction I. The colorless, thin, viscous liquid is completely saturated to bromine.

0.1421 g. substance gave 0.4479 g. CO_2 and 0.1804 g. H_2O
0.1747 g. substance gave 18.19 g. benzene, $\Delta = 0.291°$
0.3033 g. substance gave 18.19 g. benzene, $\Delta = 0.506°$

4,6-dimethylhexahydrocymene $C_{12}H_{26}$ calculated	C 84.7	H 15.3%	mol. wt. 170
$C_{12}H_{24}$ calculated	C 85.61	H 14.38%	mol. wt. 168
found	C 85.96	H 14.21%	mol. wt. 168; 168

Density $d_4^{15} = 0.8318$ $n_D^{20°} = 1.45747$; $M_D = 55.1$
Molecular refraction for $C_{12}H_{24}$ calculated M_D 55.4

Fraction II, a pale yellow, somewhat thick oil was distilled again in high vacuo. The following fractions were then obtained and studied:

Fraction IIa: boiled 115–135° at 0.3 mm.; colorless oil, saturated to bromine.

0.0734 g. substance gave 0.2325 g. CO_2 and 0.0882 g. H_2O
0.1254 g. substance gave 20.01 g. benzene, $\Delta = 0.145°$
0.2994 g. substance gave 20.01 g. benzene, $\Delta = 0.323°$

Hydrogenated trimethylated sesquiterpene

$C_{18}H_{38}$ calculated	C 85.0	H 15.0%	
$C_{18}H_{34}$ calculated	C 86.40	H 13.60%	mol. wt. 250
found	C 86.39	H 13.45%	mol. wt. 220; 236

Fraction IIb, boiled 135–155° at 0.3 mm.; yellowish, thick oil, saturated to bromine.

0.1239 g. substance gave 0.3930 g. CO_2 and 0.1521 g. H_2O
0.1484 g. substance gave 20.14 g. benzene, $\Delta = 0.128°$
0.3678 g. substance gave 20.14 g. benzene, $\Delta = 0.319°$

$C_{24}H_{50}$ calculated C 85.2 H 14.8%
$C_{24}H_{46}$ calculated C 86.23 H 13.77% mol. wt. 334
found C 86.51 H 13.74% mol. wt. 294; 292.

According to the analyses and the molecular weight determination, this fraction represents a mixture of hydrogenated, methylated sesquiterpenes and diterpenes.

Fraction III was not studied further.

The high molecular hydrogenation product precipitated with alcohol and insoluble in acetone, was purified by dissolving a little ether and precipitating with acetone, and drying at 100° to constant weight *in vacuo*.

0.1561 g. substance gave 0.4916 g. CO_2 and 0.1910 g. H_2O
0.1568 g. substance gave 0.4947 g. CO_2 and 0.1916 g. H_2O
Hydromethylrubber $(C_6H_{12})_x$ calculated C 85.61 H 14.39%
found C 85.89; 86.04 H 13.69; 13.67%

0.0695 g. substance, 18.46 g. benzene, $\Delta = 0.034°$
0.2131 g. substance, 18.46 g. benzene, $\Delta = 0.107°$
$(C_6H_{12})_6$ calculated mol. wt. 504
found mol. wt. 565, 550

This acetone-insoluble hydrogenation product is also a mixture. By fractional precipitation (solution in much ether and partial precipitation with acetone) it was possible to isolate a product with higher average molecular weight.

0.1696 g. substance gave 0.5367 g. CO_2 and 0.2052 g. H_2O
$(C_6H_{12})_x$ calculated C 85.61 H 14.39%
found C 86.30 H 13.54%

0.3244 g. substance, 19.61 g. benzene, 0.092°
0.0860 g. substance, 19.61 g. benzene, $\Delta = 0.024°$
$(C_6H_{12})_{11}$ calculated mol. wt. 924
found mol. wt. 920, 932

In a further reduction experiment with methylrubber, products of similar composition were obtained. Since less substance was used than in the first experiment, the hydrogenation proceeded more quickly and the heat decomposition and cyclicization were retarded, so that without the reduction mixture being specially fractionated higher molecular products were obtained, whose analyses agreed better with completely hydrogenated methylrubber:

0.1744 g. substance gave 0.5485 g. CO_2 and 0.2228 g. H_2O
0.1652 g. substance gave 0.5184 g. CO_2 and 0.2095 g. H_2O
$(C_6H_{12})_x$ calculated C 85.61 H 14.39%
found C 85.77; 85.58 H 14.29; 14.20%

0.1204 g. substance, 16.38 g. benzene, $\Delta = 0.038°$
0.1666 g. substance, 16.38 g. benzene, $\Delta = 0.052°$
$(C_6H_{12})_{12}$ calculated mol. wt. 1000
found mol. wt. 987, 998

All these high molecular hydrogenation products resemble hydrorubber in their physical and chemical behavior, except that they are somewhat less viscous, corresponding to their smaller average molecular weight.

η_r in 0.5-mol. tetralin solution = 1.22,[18] from which $\frac{\eta_{sp}}{c} = 0.44$

$$K_m = \frac{\eta_{sp}}{c} = 4.4 \times 10^{-4}$$

a K_m value of 3×10^{-4} was found[19] for hydrorubber.

Hydrogenation with Nickel in the Absence of Solvent

Ten grams of finely divided methylrubber were mixed with an equal amount of nickel catalyst and reduced in the autoclave at 260°–270° and 90 atm. hydrogen pressure. The reduction, which commences at 260°, is very lively, and is manifest by a rapid increase in the temperature to 295°. It is continued for two hours more at 270° and after cooling the reaction product is dissolved in ether, filtered off from the catalyst, and purified by precipitating twice from ether-acetone and ether-alcohol. The yield is only about fifty per cent, while the remainder separates as a distillable oil from the precipitating liquid on the addition of water. The hydromethylrubber is easily soluble in hydrocarbons, ether, chloroform, and carbon tetrachloride, and insoluble in acetone and alcohol. It is a viscous, colorless liquid which cannot be distilled without decomposition, and which is stable toward hot nitric acid, potassium permanganate, and bromine in carbon disulfide.

0.1578 g. substance gave 0.4956 g. CO_2 and 0.2023 g. H_2O
0.1290 g. substance gave 0.4050 g. CO_2 and 0.1674 g. H_2O
$(C_6H_{12})_x$ calculated C 85.62 H 14.38%
found 85.65; 86.62 H 14.35; 14.52%

0.2460 g. substance, 13.20 g. benzene, $\Delta = 0.062°$
0.1564 g. substance, 13.20 g. benzene, $\Delta = 0.038°$
$(C_6H_{12})_{20}$ calculated mol. wt. 1680
found mol. wt. 1530, 1590

$d_4^{16} = 0.8770$, $n_D^{16} = 1.4844$ M_D calculated 27.71, found 27.46.

References

[1] See Part 29, preceding.

[2] *Thesis* by Brunner, Zürich, **1926.**

[3] *Thesis* by Geiger, Zürich, **1926.**

[4] *Thesis* by Huber, Zürich, **1926.**

[5] *Ber.*, **49,** 55 (1916); *Ibid.*, **57,** 142 (1924).

[6] Staudinger, *Ber.*, **57,** 1205 (1924).

[7] Staudinger and Geiger, *Helvetica Chim. Acta*, **9,** 549 (1926).

[8] Large quantities of methylrubber were put at our disposal for these investigations by the Directors of the Elberfeld Farbwerke and the Badische Anilin- und Sodafabrik in Ludwigshafen. At this time we wish to express our best thanks for their kind assistance in our work.

[9] Staudinger, Geiger, Huber, and Schaal, Part 26 (1930).

[10] For the instability of rubber chains, see Staudinger and Rheiner, *Helvetica Chim. Acta*, **7,** 25 (1924); Staudinger, *Ber.*, **57,** 1203 (1927); Staudinger and Bondy, *Ann.*, **468,** 5 (1929); Staudinger and Joseph, *Ber.*, **63,** 2888 (1930).

[11] The composition of synthetic rubbers does not entirely agree with the above formula. In the first place the union of the butadiene residues is not only in the 1,4 position, but also in the 1,2 position, and in the second place synthetic rubbers are not composed of simple fibre molecules, but during the polymerization process a weak linkage of the chain formation to 3-dimensional molecules results, upon which the insolubility depends. Substances with 3-dimensional macromolecules are no longer soluble but can only swell; however the chief part of the molecules of synthetic rubbers may be constituted according to the above formula.

[12] von Braun, *Ann.*, **436,** 299 (1924); **445,** 201 (1925); **458,** 102 (1927).

[13] Accordingly butadiene-rubber, the synthetic product, is more stable than rubber itself, the natural product.

[14] See Part 26.

[15] See Part 29.

[16] *Ber.*, **54,** 360 (1921).

[17] Fierz-David, "Farbenchemie," **1922,** page 215.

[18] Additional measurements by Schwalbach, Freiburg, i. B.

[19] Staudinger, *Kolloid-Z.*, **51,** 71 (1930); Staudinger and Nodzu, Part 27. In the polyprene series the constant K_m is 3×10^{-4} (see Staudinger and Bondy, *Ber.*, **63,** 734 (1930)).

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An Investigation of the Effect of Gas Black on Rubber

P. Stamberger

DELFT

During the past year a number of studies have appeared on the causes of the reënforcing action of gas black, but it is still not possible to draw conclusions from this work. An attempt is made in the following article to find methods which will help to explain the nature of the forces which cause the reënforcing action. The experiments of other investigators have been repeated to prove whether they could be reproduced. The results described are concerned with raw rubber, for no experiments were carried out with vulcanized rubber.

Review of the Literature

Rubber-gas black mixtures are quite different from simple physical mixtures in two respects; first in their behavior upon solution, and second, in their physical properties such as strength and elasticity. Their behavior when dissolved and the properties of the resulting solutions were described by Twiss,[1] Le Blanc and Kröger,[2] Hock,[3] Blow,[4] and the writer.[5] In America there have been several publications by Depew[6] and by Sebrell and Carson.[7]

Twiss and Le Blanc and Kröger found that mixtures with high content of gas black no longer go into solution, and behave like vulcanized rubber. Le Blanc and Kröger found in addition that solutions made up of rubber with different types of gas black show a rise in viscosity with increasing content of gas black, contrary to rubber solutions. The author was able to confirm this behavior. It was further found that if these gas black mixtures are covered with the solvent immediately after milling, they can still be dissolved.

After standing a few days, they can no longer be dispersed.[5] Blow[9] found these changes after standing while studying the viscosity of these mixtures. He proved that upon standing the viscosity increases greatly, and he also observed in mixtures which had been standing the appearance of elastic properties which are barely evident in the solutions prepared immediately after milling. Furthermore, Blow was able to prove that there is a slight increase in the viscosity of solutions of masticated rubber upon standing. This was, however, much smaller than the differences which were found with mixtures containing gas black.

It is therefore proved beyond question that a rubber mixture changes upon standing. The fact that this insolubility occurs for the greater part only upon standing renders improbable the explanation of Depew[10] that the insolubility is a result of the flocculation of the filler particles which surround the rubber and which are supposed to form a network about it. It is very improbable that such a structure would form in the highly viscous rubber medium on standing in the cold. Moreover, the action of the swelling agent would not form such a flocculated structure, because in this case no soluble mixtures could be found.

Depew found no parallelism between plasticity and insolubility, and he could not find any change in the plasticity of the mixture upon standing. From the changes which have been noticed upon standing (insolubility, viscosity, heat of swelling) one would expect a change in the plasticity.

The importance of the discovery of Hartner[11] that the heats of swelling of rubber

and of rubber–gas black mixtures during standing change greatly is very difficult to judge, since this change was not followed along with that of the raw rubber employed, and therefore it is not established how much this increase depends upon the presence of the gas black. It is very interesting that the same values were found after evaporation of the solvent, but it makes it improbable that a crystallization would take place upon standing, and the heat tone measurement might represent in part a heat of fusion.

The uncertainty of drawing definite conclusions upon the work of rupture from the calorimetric measurements is still greater because it is very difficult to prove that raw rubber has the same heat of swelling after admixture of the gas black. The further uncertainty that the measured values correspond only to the change of total energy (therefore are *U*-values), and that the proportion of the free energy (*A*) was assumed arbitrarily to be only 0.5, is also indicated by Hartner.[12] Any conclusions drawn from calorimetric measurements based on experimental data available today must be made with caution.

In explaining the reënforcing action of the filler, Blake[13] assumed that the adhesion between the rubber and the particles of filler is greater than that between rubber and rubber itself. This assumption agrees in principle with the facts found in testing the adhesion of various adhesives, namely, that the strength of these places exceeds that of the original substance. In such cases an orientation of the molecules of the adhesive was assumed according to the idea of Hardy and of McBain[14] and this was applied to rubber. The reënforcing effect not only depends upon the boundary surface tension between rubber and filler, but it also depends upon the formation of a strong rubber matrix of increased strength resulting from a change in the structure of the rubber. Since most fillers reënforce rubber to any significant extent only when it is in the vulcanized state, it is also probable that the structure formed during vulcanization is greatly influenced by the fillers.

According to Depew himself, there is still the possibility that if the plasticity is not changed the formation of a new structure is indicated by the change in solubility, though this structure is much weaker than that destroyed by mastication, and is not detected by the crude methods of plasticity determinations.

According to the present state of this problem it may be said without hesitation that a specific effect of gas black on rubber is well established and that the mixtures change upon standing. Furthermore, the assumption may be considered as proved that the reënforcing effect is to be attributed to the boundary surface tension between rubber and gas black, as a result of which the properties of the rubber matrix are also altered.

Plasticity and Solubility of the Mixtures

In this experiment "Micronex" gas black was used. In order to measure the plasticity, mixtures were prepared with increasing contents of gas black, and these were studied with the Williams plastometer various times after mixing. In the mixing of the gas black conditions were kept constant as nearly as possible.

A large quantity of first latex crepe was milled and 100 grams were taken for each batch. The temperature of the rolls varied from 35° to 40° C. (the rolls were cooled). The speeds of rotation of the rolls were 38 and 56 r. p. m., and their diameter was 12.5 cm. The raw rubber was first milled for 5 min., the gas black was added within 15 min., and the mixture allowed to run an extra 5 min. on the rolls. Three and five-tenths grams of the finished batch were put in the plastometer immediately to determine the plasticity, and after one hour (at which time the temperature of the plastometer was assumed to be 70° C.) the plasticity was read. Spherical test pieces were used, and the thickness of the disc after 30 min. was

chosen as a measure of the plasticity. The load on the plastometer was five kilograms. Measurements were also made at 50° C., and the results were quite parallel to those at 70° C. The determinations were repeated after various intervals. The data are given in Table I.

TABLE I

(Determined at 70° C.)

Gas Black Content, %	Immediately	Pressure of the Disc after 30 Minutes 7	30	70	90 Days
0	2.0	2.0	2.1	2.1	2.1
5	1.8	1.7	1.9	1.8	1.8
10	2.0	1.9	2.2	1.9	1.9
15	2.3	2.1	2.5	2.3	2.2
20	2.6	2.4	2.6	2.5	2.5
30	3.3	3.3	3.1	3.5	3.5
40	4.2	4.2	4.3	4.4	4.4
(Determined at 50° C.)					
0	2.9	2.8	2.8		
5	2.6	2.6	2.6		
10	2.9	2.8	2.9		
15	2.8	2.8	2.9		
20	3.2	3.3	3.4		
30	3.9	3.8	3.8		
40	4.5	4.5	4.7		

It is evident that up to 20 g. of gas black to 100 g. of rubber the plasticity changes very little with increase in the content of the gas black. The plasticity of rubber milled 20 minutes under the same conditions as the gas black mixtures was less. When, however, the rubber was recovered from these gas black mixtures by swelling and diffusion, and its plasticity was measured after drying, it was found to be considerably greater. In this way it was proved that the addition of gas black heightens the effect of milling. This was also proved by Blow[15] in viscosity measurements.

A change (decrease) in the plasticity upon standing was observed in mixtures which were milled for a longer time. This can be seen from the original plasticity values. These mixtures were milled for 15 minutes longer after the addition of the gas black, instead of 5 minutes. Table II gives these values.

TABLE II

Gas Black Content, %	Immediately	Thickness of Disc at 70° C. Measured after 1 Day	2 Days	14 Days
0	0.8	0.8	0.7	0.7
20	1.3	1.7	1.5	1.7
30	2.0	2.1	2.4	2.4
40	2.6	3.1	3.3	3.4
60	3.2	4.6	4.8	4.8

It may be concluded without further question that the greater the content of gas black the greater was the decrease in plasticity upon standing. In a few cases changes in the plasticity could still be observed independent of the influence of the very severe milling. These changes were, however, very irregular, and their cause was not proved conclusively.

The addition of softeners had very little effect on the behavior of the mixtures. Samples prepared with 5 g. of stearic acid to 100 g. of rubber, treated like those described in Table I, gave a higher initial plasticity value, but there was likewise no change upon standing. The values obtained are given in Table III.

TABLE III

Gas Black Content, %	Thickness of Disc at 79° C. Measured after Immediately	1 Day	7 Days
30	2.7	2.9	2.8
40	3.4	3.4	3.5

When all these mixtures were immersed in benzene after various times of standing, their behavior differed. When they were dissolved after increasing times of milling, the change in solubility depended on the content of gas black. The solubility was also dependent upon the degree of mastication, as has been described by Depew.

The fact that the mixtures become insoluble only after standing makes improbable the explanation of Depew that a semi-permeable membrane is formed around the rubber by the gas black particles. In a highly viscous medium of the type of rubber mixtures hardly any change in the dispersion of the gas black can be expected to take place upon standing, and therefore no membrane would be formed. Probably this is another kind of cohesion between the rubber particles, the structure of which we still know little about. The mixtures prepared with stearic acid behaved in a similar way, becoming insoluble after a short time. This is contrary to the concept of Blake,[16] according to which the stearic acid is adsorbed by the gas black particles from the rubber in the dissolved state, so that in this way a boundary surface of rubber–stearic acid–gas black is formed. If this were the case, benzene should dissolve out the stearic acid, causing a dispersion of the mixture. However, this was not the case, in contrast to observations with zinc oxide.

About two days after contact with the solvent equilibrium was reached, and after two months there was practically no further change. In this way three characteristic conditions were established:

1. The whole system forms a homogeneous solution.
2. Part of the mixture dissolves and colors the liquid black, whereas the greater part remains as a piece of definite shape.
3. The mass remains in the undispersed state and the liquid remains uncolored.

Table IV which follows gives the changes in the capacity to disperse of the gas black mixtures. The data show the appearance of the mixtures one week after they were placed in the solvent, in which condition they remained for a longer time (for a month). The appearance is shown by the numbers 1, 2, and 3.

TABLE IV

A. (The plasticity of the mixtures has been shown in Table I)
5 cc. of the mixture was combined with 100 cc. of benzene

Content of Gas Black	Capacity for Dispersion Time of Solution after Milling At Once	7 Days	14 Days
5	1	1	1
10	1	2	3
15	1	2	3
20	1	3	3
30	2	3	3
40	3	3	3
B. (Plasticity shown in Table II)			
20	1	1	2
30	1	2	3
40	2	3	3
60	3	3	3
C. (Mixture containing stearic acid. Plasticity shown in Table III)			
30	2	3	3
40	3	3	3

These measurements lead to the following conclusions:

1. A parallelism does not exist between plasticity and dispersibility of the mixtures.

2. The capacity for dispersion changes upon standing, and the extent of this change depends upon the degree of milling as well as upon the content of gas black.

The Problem of the Adsorption of Rubber on Gas Black

It had been observed previously and again in the course of these experiments in many cases that, although the rubber mixtures containing gas black did not disperse, part of the rubber in them migrated into the solvent above them in the swollen mixture, and in this way became separated from the gas black.

Moreover, it is already known that gas black can be dispersed to a high degree by shaking with a rubber solution, and this can be accomplished with the pure solvent only with certain kinds of gas black. This dispersed black can no longer be separated by sedimentation or centrifuging from its suspension.[17] It has been proposed to evaluate gas blacks by their adsorptive power for dissolved chemical compounds (and iodine solution).[18]

The following study was made to establish whether there is an adsorption of rubber on gas black when (1) a rubber solution is agitated with gas black, and (2) when a rubber-black mixture is covered with solvent and allowed to stand until equilibrium is reached.

In the first case the concentration of the rubber in the solution would have to decrease with the commencement of adsorption after shaking. In the second case the concentration of the rubber in the supernatant liquid would be less than in the jelly itself after equilibrium is reached.

It has been shown that in the first case part of the gas black is very finely dispersed in the rubber solution; however, the concentration of the rubber was practically unchanged after the separation of the gas black. In this case in order to determine the relative surface areas, the heat of wetting was measured when the gas black was covered with benzene and when it was covered with a rubber solution. The amount of gas displaced during the wetting was also measured. In both cases the same values were obtained, which indicates that the surfaces taking part in the wetting are the same. The formation of a suspension therefore cannot be explained by a better wetting with a rubber solution.

It was established in the second case, that if the mixture does not disperse the diffusion with increasing black content was much slower, and yet after equilibrium was reached the concentration of the rubber in solution was the same as that of the jelly itself. If the solvent containing the rubber is removed and replaced with fresh solvent, enough rubber will again diffuse so that the concentration becomes the same. If this is repeated, the black as well begins to disperse with the rubber. This phenomenon may be regarded as an indication that in spite of the influence of the solvent there is still an attraction between the rubber and the black. Nevertheless, it was not possible in this way to study the adsorption of black by rubber quantitatively. The qualitative results probably indicate, however, an attraction between the rubber and the black.

The determination of the heat of wetting was made in a Bunsen ice calorimeter. Samples from various lots of "Micronex" gas black were studied. It was found that the blacks always gave the same heat of wetting, which indicates great uniformity in the products. In every determination five to six grams of black, dried at 110° C., were used. Toluene was used as the wetting liquid. Table V gives the values obtained.

TABLE V

Gas Black	Heat of Wetting in Calories for 1 Gram Gas Black in Toluene	Rubber Solution
1	4.2	4.1
2	3.9	3.9
3	4.2	4.0

An attempt was first made to calculate the amount of gas displaced by the solvent from the difference in the gas pressure before and after the wetting. For this purpose a flask of about 200 cc. content furnished with a manometer was used. The gas black was introduced into the previously dried flask and a glass tube containing the toluene was inserted. The whole apparatus was placed in a thermostat and allowed to remain until a constant temperature was reached (*i. e.*, until there was no longer any difference in the gas pressure). The flask was then so turned that the toluene could flow over the black. An effervescence of the liquid was observed at once and, because of the gas evolved, the pressure rose from 8 to 10 g. per cc. In rubber solutions which are highly viscous the escape of the gas bubbles can be watched for several minutes. The method is not suitable, however, for quantitative mixtures, since after a certain time the pressure diminished and became constant only after ten to twelve hours. Apparently part of the liberated gas is again dissolved. It was, therefore, found preferable to determine the escaping gas by direct volumetric measurement. The flask, equipped in the manner described, was connected with a eudiometer, with which the volume of the escaping gas was measured. In these measurements 5 to 6 grams of black and 10 to 15 cubic centimeters of toluene were added. Table VI gives the values obtained.

TABLE VI

Wetting Liquid	Quantity of Escaped Gas in Cc. per 1 G. Black at 750 Mm. Hg Pressure
Toluene 1	1.8
Toluene 2	1.6
Rubber solution (5%) 1	2.0
Rubber solution (5%) 2	1.7

These results show that the dispersing action of a rubber solution does not depend upon a better wetting. This phenomenon cannot yet be explained.

Summary

1. It is shown that changes in the solubility of mixtures of rubber and gas black do not parallel changes in plasticity.

2. Rubber-gas black mixtures become insoluble only upon standing after milling, which makes it improbable that the insolubility of these mixtures depends upon a flocculation of the gas black in the mixture.

3. An adsorption of rubber from its solutions by gas black could not be established.

4. The heat of wetting of gas black with toluene and of a five per cent rubber solution in toluene were the same, as was the quantity of gas set free by the wetting. The dispersing action of rubber solutions does not depend upon a better wetting.

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Mastication. A Preliminary Study

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[Through lack of space it is necessary to omit a detailed review and discussion which forms the first part of this paper (on pages 487–501 of the *Transactions*).]

The Mastication of Rubber in Various Gases

Experimental.—It was thought that much light could be thrown upon the mechanism of mastication by conducting experiments in an internal mixer through which were passed various gases.

The machine employed in the work to be described was a small internal mixer, capable of taking about 1000 grams of rubber. Much difficulty was experienced in making the mixer gas-tight, but it was finally achieved by removing the original lid and fixing with Chatterton's compound one made from thin tinned sheet. This was held in position by covering with a sheet of vulcanized rubber also cemented down by the same compounds and fastened with several screws passing through to the body of the machine. Holes were bored through this improvised lid for rubber tubes conducting gases to and from the mixer, the tubes being cemented into the lid by means of a quick curing solution. An oblong hole was cut in the rubber cover, through which a charge of rubber could be introduced and removed. An oblong vulcanized slab was used to fill this hole during the experiment; and after trials with various materials, putty was found the most efficient substance to produce a gas-tight joint.

The procedure adopted was to introduce through the hole in the lid 300 grams of pale crepe rubber torn into shreds. Cold water was circulated through the jacket of the machine in order that the rubber should be masticated under the most severe conditions and also to prevent the heat generated during mastication from softening the Chatterton's compound used in fixing the lid. A charge of rubber considerably smaller than the normal capacity of the machine was employed in order that the motor should not pull up when starting the experiment. Preliminary experiments showed that with more than 300 grams of rubber great difficulty was experienced in commencing mastication. In the usual way rubber wou d be introduced in small quantities in order to give the machine a chance to soften the first pieces before filling the chamber; but in the investigation undertaken it was essential that the mixer should be fully charged at the commencement so that the rubber should be masticated from the beginning in the gas under test.

At intervals during mastication the machine was stopped and a small piece of rubber removed for plasticity determination, the cover being afterward replaced and the gas allowed again to fill the chamber before mastication was resumed. In some of the longer experiments the cover was not taken from the mixer until the completion of the run. In order to ensure minimum admixture of the gas with air, a manometer was attached to the mixer, and a pressure of gas equivalent to between 7 and 14 centimeters of water was maintained within the mixer throughout the experiment to promote flow of gas out from the glands rather than leakage of air into the machine.

The plasticity of the rubber after mastication was determined in a Williams plastometer of the modified type recommended by the Rubber Research Association, the plastometer being placed in a water-heated oven maintained at a temperature of 70°. Two cc. pellets of rubber weighing 1.86 grams. were cut and placed

in the oven for 10 minutes before making a determination. After reaching the temperature of the oven, a pellet was placed between two cigarette papers 0.001 inch thick and put on the lower plate of the plastometer. The upper parallel plate loaded with 5000 grams was then lowered on to the ball of rubber and the thickness noted at intervals of three minutes as the pellet squeezed out under pressure. In the earlier experiments the plasticity was calculated for each individual test by applying the formula $K = YX^n$.

Where K is the plasticity,
Y is the thickness of the pellet in millimeters,
X is the time in minutes, and
n is a constant which Williams states depends upon the plastometer.

Throughout the experiments the value of n in the above equation was found to vary with the time of mastication, though for any particular masticated sample it was practically constant. With tough rubber retaining much of its original nerve, n in the above equation had a value ranging from 0.06 to 0.10; while, for samples thoroughly softened by mastication, the value increased to approximately 0.30 (the accepted value is in the neighborhood of 0.196).

In finally plotting the results for presentation, therefore, it has been found more convenient to consider the thickness of the pellet of rubber after a definite period of 9 minutes in the plastometer as being a measure of the plasticity of the rubber. The determination of recovery values due to elastic after-effect, as made by Grenquist (*Ind. Eng. Chem.*, **22**, 759 (1922)) was not practicable with the plastometer used in this investigation.

Results

A. Mastication in Air.—As a preliminary experiment, 300 grams of pale crepe rubber were masticated in the cold mixer with the lid removed so that air had free access. The plasticity rapidly increased, and at the end of 2 hours the rubber was very soft and sticky. The results are given in Table A, and plotted in the graph (Fig. 1). After an hour's mastication the development of a characteristic acrid odor was noticed, suggesting the formation of some acidic or aldehydic oxidation product.

It is to be noted that the value of n in the plasticity equation $K = YX^n$ gradually increases from 0.1316 after 15 minutes' mastication to 0.2672 after 105 minutes' mastication.

TABLE A

MASTICATION IN AIR

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X = 3 Min.	6 Min.	9 Min.	n Calculated	Plasticity K ($K = YX^n$) Calculated for $X = 6$
15	5.050	4.620	4.370	0.1316	5.848
30	2.725	2.430	2.265	0.1682	3.286
45	1.545	1.320	1.240	0.2000	1.889
60	1.270	1.090	0.995	0.2221	1.624
75	1.095	0.940	0.860	0.2196	1.393
90	0.960	0.800	0.720	0.2620	1.279
105	0.815	0.680	0.6075	0.2672	1.098
120	0.910	0.775	0.725	0.2070	1.123

B. Mastication in Nitrogen.—The nitrogen was carefully purified from oxygen by bubbling through a 2-ft. column of concentrated alkaline pyrogallol solution.

The gas was then dried by passing through a wash bottle of concentrated sulfuric acid before admission to the mixer. Several repeat experiments were made, and in each case the rubber softened exceedingly slowly showing hardly any visible sign of mastication after one hour in the mixer. The value of n in the plasticity equation $K = YX^n$ remained low throughout the experiment; which seems characteristic of a nervy resilient rubber. The plasticity remained low. It was found that the greater the precautions taken to exclude air, the tougher the rubber remained; and therefore in some of the longer mastications the lid of the machine was not removed until the completion of the experiment. No acrid odor whatsoever was produced throughout the experiment with nitrogen, the rubber retaining a slight nutty smell.

Experiment B1.—Three hundred grams of pale crepe masticated in nitrogen with cold water passing through jacket of mixer. Nitrogen was admitted for 30 minutes before commencing mastication. After removing small samples of rubber for

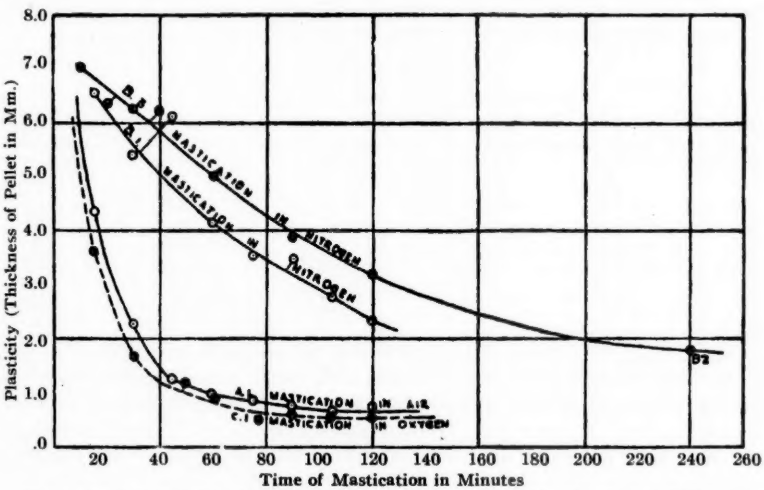

Figure 1—Relationship between Plasticity and Time of Mastication in Different Gases

plasticity test, nitrogen was passed through the mixer for at least five minutes before recommencing mastication.

TABLE B1

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X = 3 Min.	6 Min.	9 Min.	n Calculated	Plasticity K ($K = YX^n$) Calculated for $X = 6$
15	7.080	6.750	6.540	0.0721	7.681
30*	5.970	5.620	5.410	0.0897	6.600*
45	6.765	6.335	6.105	0.0933	7.487
60	4.490	4.250	4.110	0.0805	4.898
75	3.955	3.680	3.525	0.1047	4.439
90	3.930	3.620	3.470	0.1133	4.435
105	3.200	2.920	2.770	0.1311	3.693
120	2.800	2.540	2.315	0.1732	3.463

* NOTE: The pellet in this case was not sufficiently spherical. The rubber was very tough to cut.

Experiment B2.—Prolonged mastication in nitrogen, keeping mixer closed until end of 4 hours. Plasticity determination made immediately after completion of mastication.

TABLE B3

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X = 3 Min.	6 Min.	9 Min.	n Calculated	Plasticity K ($K = YX^n$) Calculated for $X = 6$
240	2.225	1.93	1.77	0.2081	2.803

Experiment B3.—The previous experiments had shown the far-reaching influence of oxygen during mastication. In experiment B3, therefore, greater care was taken to exclude air during mastication in nitrogen. Nitrogen gas was passed through the mixer for 15 minutes before commencing mastication, a good positive pressure was maintained in the machine during the mechanical working of the rubber, and nitrogen was passed for 10 minutes before restarting the motor after removing a sample of masticated material for plasticity test.

TABLE B3

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X = 3 Min.	6 Min.	9 Min.	n Calculated	Plasticity K ($K = YX^n$) Calculated for $X = 6$
10	7.73	7.28	7.04	0.0851	8.480
20	6.88	6.50	6.33	0.0759	7.447
30	6.75	6.45	6.27	0.0671	7.274
40	6.70	6.415	6.24	0.0648	7.204
60	5.53	5.205	5.02	0.0880	6.094
90	4.235	4.03	3.87	0.0819	4.668
120	3.60	3.34	3.185	0.1112	4.078

C. Mastication in Oxygen.—The experiments in section B proved that the breakdown of rubber during mastication in nitrogen was much slower than during mastication under similar conditions in air. It was therefore natural to inquire whether mastication would be more rapid in pure oxygen than in air. Three hundred grams of pale crepe were therefore masticated as before while a stream of dry oxygen was passed through the mixer.

TABLE C1

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X = 3 Min.	6 Min.	9 Min.	n Calculated	Plasticity K ($K = YX^n$) Calculated for $X = 6$
15	4.16	3.81	3.61	0.1291	4.804
30	2.115	1.82	1.675	0.2125	2.663
50	1.51	1.32	1.22	0.1941	1.869
62	1.165	0.995	0.905	0.2301	1.503
77*	0.68	0.56	0.495	0.2818	0.940
90	0.795	0.68	0.615	0.2340	1.034
105	0.76	0.65	0.59	0.2300	0.9817
120	0.71	0.59	0.535	0.2572	0.9356

* NOTE: After one hour's mastication in oxygen the rubber became so soft that experimental error in determination of the plasticity was great. The pellet squeezed out to a large thin disc, the thickness of which had a tendency to vary slightly in different places owing to imperfect parallelism of the plastometer plates.

Experiment C2.—A further 300 grams of pale crepe rubber were masticated in oxygen, dried by passing through sulfuric acid, with cold water in the jacket of the mixer. The plasticity tests on this repeat experiment were made after the masti-

cated rubber had stood for 2 hours. The results were almost identical with those given in Table C1.

D. Mastication in Ozonized Air.—Rubber normally oxidizes very slowly in air; hence it seemed remarkable that mere mechanical working should cause oxygen to have such a profound effect on the physical properties of rubber. It was thought probable that the static electric charges produced on the rubber during mastication gave rise to ozone, which was the effective agent in bringing about the changes associated with mastication

An electric blower was therefore connected with the apparatus; and by its aid a steady stream of air was blown into the mixer through an ozonizer tube attached to a powerful induction coil, at such a rate as to maintain a pressure equivalent to 13 cm. to 14 cm. water in the machine throughout mastication.

Table D1

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X =		
	3 Min.	6 Min.	9 Min.
15	3.30	3.00	2.805
30	2.475	2.12	1.98
45	1.60	1.43	1.32
60	1.19	0.96	0.86
75	1.19	1.045	0.965
90	1.03	0.89	0.79
105	0.905	0.785	0.70
120	0.89	0.80	0.69

E. Mastication in Ozonized Oxygen.—The results obtained with ozonized air (Table D1) were not greatly different from those given with air alone. It was decided to masticate 300 grams of pale crepe in a cold mixer through which ozonized oxygen was passing. During this experiment the rubber tube connections to the masticating machine repeatedly cracked and had to be repaired. The plasticity tests were made a few hours after completion of the experiment.

Table E1

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X =			n Calculated	Plasticity K ($K = YX^n$) Calculated for $X = 6$
	3 Min.	6 Min.	9 Min.		
10	7.10	6.575	6.28	0.117	8.032
20	6.27	5.60	5.22	0.1667	8.072
30	5.85	4.57	4.40	0.259	7.269
45	3.00	2.77	2.64	0.1162	3.412
60	2.47	2.29	2.19	0.1095	2.786

The rubber masticated in ozonized oxygen in experiment E1 remained remarkably tough, being far less broken down than was the case with mastication in pure oxygen (Expts. C1 and 2), and considerably tougher than that masticated in air (Expt. A1). This astonishing result was the reverse of what was expected.

During this first mastication in ozonized oxygen the rubber tube connection between the ozonizer and the internal mixer repeatedly cracked and had to be repaired by shortening and wrapping with adhesive tape.

The experiment was therefore repeated by substituting a glass tube for the rubber connection between the ozonizer and the mixer. Dry ozonized oxygen was passed during mastication for one hour in the mixer with cold water in the jacket, and a plasticity test was made on the rubber immediately it was removed from the machine. The plastometer readings are given in Table E2. It will be noted that

in this experiment the rubber became much softer than in Expt. E1; in fact, the plasticity was comparable with that after 60 minutes' mastication in dry oxygen (cf. C1 and 2).

TABLE E2

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X =		
	3 Min.	6 Min.	9 Min.
60	1.15	0.995	0.895

The experiment was repeated, removing samples for plasticity tests at intervals up to 2 hours. The results are given in Table E3

TABLE E3

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X =		
	3 Min.	6 Min.	9 Min.
15	3.635	3.28	3.075
30	1.95	1.695	1.57
45	1.375	1.20	1.105
60	0.86	0.73	0.63
75	0.74	0.54	0.475
105	0.50	0.405	0.345
120	0.62	0.50	0.43

These results differ but little from those obtained when the mastication was carried on in pure oxygen (Tables C1 and 2). The experiment was again repeated with the following results (Table E4).

TABLE E4

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X =		
	3 Min.	6 Min.	9 Min.
10	5.955	5.445	5.02
20	3.395	3.075	2.90
30	2.70	2.335	2.20
40	1.85	1.665	1.495
60	1.18	1.02	0.92
90	0.915	0.79	0.725
120	0.66	0.56	0.50

It remained to explain the anomalous results obtained in Expt. E1, when mastication in ozonized oxygen produced little softening of the rubber. The only alteration in the conditions was that the vulcanized rubber tube connection between the ozonizer, and the machine in Expt. E1 was replaced by a glass tube in experiments E2, 3, and 4. It was thought possible that some volatile product of the vigorous reaction of the ozone on the rubber tubing used in Expt E1 might have retarded mastication; and it was decided to repeat the mastication in ozonized oxygen using a rubber delivery tube. A fresh length of rubber tubing was therefore connected between the ozonizer and the masticator, and mastication continued until the tubing failed. The results are given in Table E5.

TABLE E5

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X =		
	3 Min.	6 Min.	9 Min.
10	7.37	6.89	6.445
20	4.08	3.74	3.535

Although this experiment did not duplicate the results of Expt. E1, it will be noted that the rubber commenced to soften much more slowly than during mastication in oxygen, or in ozonized oxygen conducted to the mixer through a glass tube.

Experiment E6.—In this experiment, ozonized oxygen was passed through a U-tube containing ground vulcanized rubber before conducting to the internal mixer; the object being to investigate the effect on rate of mastication, of the aldehydic volatile products produced by the action of ozone on vulcanized rubber. Almost no ozone remained in the oxygen entering the mixer, but the gas had a strong acrid odor resembling that produced on prolonged mastication of rubber in air or oxygen.

The results are indicated in Table E6. Comparing them with those in Tables A1 and C1 it is seen that the volatile aldehydic products retarded mastication; especially during the initial stages.

TABLE E6

Time of Mastication in Minutes	Thickness Y of Pellet in Mm. after X Min. in Plastometer, Where X =		
	3 Min.	6 Min.	9 Min.
15	6.41	5.42	4.92
30	2.615	2.33	2.175
45	1.79	1.57	1.455
60	1.555	1.35	1.24
75	1.265	1.09	1.00

F. Change in Weight during Mastication.—As oxygen had proved to play such an important role in mastication it seemed desirable to investigate what change in weight, if any, takes place during normal mastication on a two roll mill.

A preliminary experiment was made by masticating approximately 50 grams of pale crepe rubber, carefully weighed on a chemical balance, on a small experimental mill, with the water-cooled rolls revolving at friction speeds of 2:1. The changes in weight after each consecutive 5-minute mastication were as indicated in Table F1. After 20 minutes on close-set rolls the rubber became too sticky to handle.

TABLE F1

Time of Mastication in Minutes	Weight of Rubber, G.	Change in Weight, G.	Total Gain in Weight, %
0	50.6103	......	......
5	50.5706	−0.0397	−0.078
10	50.6025	+0.0319	−0.015
15	50.6689	+0.0664	+0.116
20	50.6947	+0.0258	+0.167

The changes in weight were sufficiently significant to warrant more careful study. A quantity of about 250 grams of pale crepe was therefore carefully weighed, in four lots, on a delicate balance and masticated on a larger mill with the rolls set just close enough to produce a bank of rubber at the nip. Friction speeds were used, and cold water was passed through the rolls during mastication. Care was taken to avoid loss, but as the rubber became more plastic there was difficulty in ensuring that none was trapped beneath the check plates at the ends of the rolls.

The results are shown in Table F2

As previously, there was an initial fall in weight, attributed to moisture being driven from the rubber, followed by a progressive gain in weight. A sample of pale crepe was therefore separated into piles and dried in a vacuum desiccator over fused calcium chloride for 6 weeks before commencing the next series of mastications, the results of which are tabulated below. The rubber lost 0.123 per cent in weight during drying.

TABLE F2

Time of Mastication in Minutes	Weight of Rubber, G.	Change in Weight, G.	Total Gain in Weight, %
0	247.3534	....	.....
10	247.2500	—0.1034	—0.042
20	247.2994	+0.0494	—0.022
30	247.4590	+0.1606	+0.043
40	247.5028	+0.0438	+0.060
50	247.6606	+0.1578	+0.124
60	247.5842(?)	—0.0764(?)	Becoming
70	247.9017	+0.3175	sticky

TABLE F3

Time of Mastication in Minutes	Weight of Rubber, G.	Change in Weight, G.	Total Gain in Weight, %
0	272.1988	......	......
10	272.3052	+0.1064	+0.0391
20	272.4092	+0.1040	+0.0773
30	272.5302	+0.1210	+0.1216
40	272.6251	+0.0949	+0.1564
50	272.6938	+0.0687	+0.1817
60	272.7534	+0.0596	+0.2033
70	272.7940	+0.0406	+0.2185
80	272.8388	+0.0448	+0.2350
90	272.8992	+0.0604	+0.2572
100	272.9650	+0.0658	+0.2811
110	273.0533	+0.0883	+0.3133
120	273.0795	+0.0262	+0.3194

Observations

1. During mastication in air and oxygen (Expts. A and C) a sour, acrid odor developed. There was no trace of this odor when the rubber was masticated in nitrogen. After 4 hours in nitrogen the rubber still had a pleasant faint nutty odor.

2. Repeat determinations of the plasticity of nitrogen masticated samples after storage for several weeks showed appreciable recovery.

3. During mastication in air or oxygen, both in the internal mixer and on the rolls, a condition was eventually reached at which the rubber assumed a whitish opalescent appearance, probably owing to the occlusion of small bubbles. This occurred after the rubber had gained about 0.24 per cent in weight. At the same time it became excessively sticky, and the rate of oxygen absorption increased (see latter part of Fig. 2).

4. During mastication on open rolls, a small quantity of ozone was produced. This was proved by withdrawing air from the "nip" through a glass tube containing filter paper soaked in starch and potassium iodide solution, from which iodine was liberated.

5. The acrid odor of the oxygen in Expt. E6, after ozonizing and passing through a column of ground vulcanized rubber, was almost identical with that evolved during prolonged mastication of rubber in air or oxygen.

6. Distilled water through which the acrid-smelling air from the internal mixer was drawn during a prolonged cold mastication of pale crepe rubber remained neutral to litmus. Ammoniacal silver nitrate did not produce a silver mirror, as might be expected in the presence of appreciable quantities of aldehydes, but resorcinol and strong sulfuric acid gave a slight positive reaction for formaldehyde.

Discussion.—The experiments described have proved conclusively that the presence of oxygen is necessary if mechanical working of rubber is to achieve that

permanent increase in plasticity characteristic of mastication. Rubber only softens very slowly when masticated in nitrogen, and does not become tacky and "killed" even after prolonged mastication in an inert gas.

The total increase in weight of dry rubber during mastication, before it becomes too sticky to handle, is 0.32 per cent (see Table F3, and Fig. 2). While admittedly this cannot represent the entire oxygen reacting (some is lost with the pungent volatile oxidation products), the amount of oxygen responsible for normal mastication is undoubtedly small. There was difficulty in ensuring that no trace of oxygen should enter the mixer through the glands during a period of several hours. Furthermore, pale crepe rubber normally contains some adsorbed oxygen. Hence it is thought probable that mastication would have no effect on the properties of raw rubber in the complete absence of oxygen.

It has already been shown by Porritt and Fry (*Trans. Inst. Rubber Industry*, **3**, 203 (1927), and Grenquist (*Ind. Eng. Chem.*, **22**, 759 (1930)) that the physical effects of mastication may be duplicated by heating rubber in air or oxygen. It is suggested

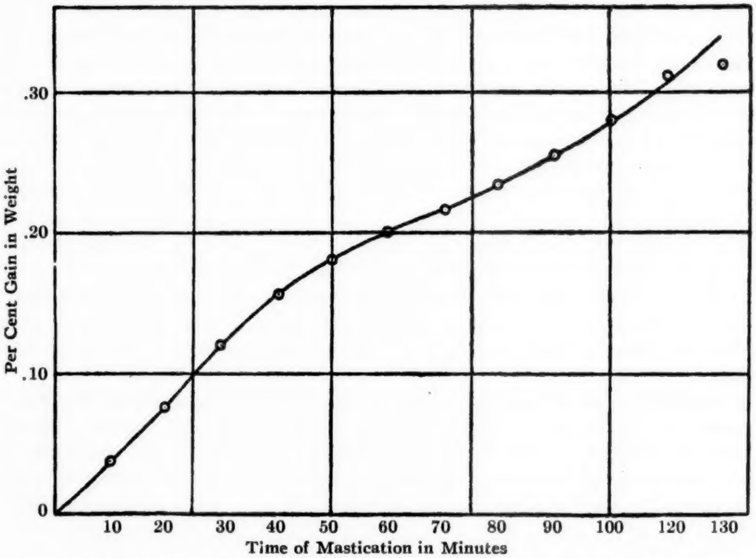

Figure 2—Gain in Weight When Dry Rubber Is Masticated in Air

that on exposure of raw rubber to the atmosphere at normal temperatures in the absence of strong light, a protective coating of oxidized rubber may be formed on the surface, preventing further rapid softening.

Alternatively, if rubber be an isocolloidal jelly—a system consisting of two phases of the same hydrocarbon in different states of aggregation, as suggested by Hauser, Pummerer, Auer, and others—it is thought that oxygen can only act quickly upon the more liquid component laid bare during mastication.

The amount of oxygen absorbed during the mastication process is small, and is consistent with the suggestion of Auer (*Trans. Inst. Rubber Industry*, **4**, 499 (1929)) that mastication is an example of gas-peptization; but the increasing absorption of oxygen as mastication proceeds (see Fig. 2) is suggestive of chemical combination. Furthermore, Auer's gas-peptization theory does not explain the formation of vola-

tile oxidation products, or the fact that rubber does not soften when subjected to mechanical working in nitrogen.

It seems more probable that rubber is a polyphase system containing a wide range of high polymers of isoprene, as suggested by Whitby (*Trans. Inst. Rubber Industry*, **5**, 184 (1929); **6**, 40 (1930)). If such be the case, there would be slippage between the separate molecules during the plastic flow caused by mastication, and a fresh surface-layer of oriented rubber molecules would continually be exposed. In such circumstances it is to be expected that some of the double bonds in the polymerized isoprene chains should be readily attacked by oxygen, leading to the production of lower rubber-like polymers; and, where the double bonds attacked were at the end of the rubber molecule, to small quantities of aldehydic or acidic substances such as formaldehyde, formic acid, pyruvic aldehyde or acid, levulinic aldehyde or acid, succinic aldehyde or acid. Some of these are definitely produced during the ozonolysis of rubber. It is significant that the odor noticed during cold mastication of rubber in air and oxygen was similar to that produced when ozonized oxygen was passed over rubber.

Ozone was found to be produced in small quantities during the mastication of rubber on open rollers; but mastication in ozonized air and ozonized oxygen led to anomalous results and did not elucidate whether ozone plays a role in normal mastication. The volatile aldehydic products of the action of ozone on vulcanized rubber have a slight retarding action on mastication. This is interesting in view of the recent work of Kohman (*J. Phys. Chem.*, **33**, 226 (1929)), who found that ozone caused a permanent change in rubber, protecting it against the action of oxygen. Kohman suggests that the action of ozone on rubber prevents the formation or accumulation of the catalyst responsible for the auto-catalytic nature of the normal reaction of rubber with oxygen. He suggests that it may be possible to improve the aging qualities of rubber by giving it an ozone treatment.

It is still probable, however, that ionization of oxygen, both on the surface and throughout the mass of rubber on a masticating mill, caused by static charges produced by friction, plays some part in promoting oxidation during mechanical working.

The present design of internal mixer employed for masticating rubber takes no cognizance of the fundamental role of oxygen in promoting plasticity. Air should have free access to the rubber during mastication; or, alternatively, the mastication should be accelerated by admitting oxygen or air under pressure during the process. It is suggested that advantage should be taken of the increased softening action of hot air by masticating at a higher temperature than is general at present.

Summary and Conclusions

1. The oxygen present during mastication of raw rubber is responsible for the increase in plasticity which normally occurs.

2. Rubber does not soften appreciably when masticated in nitrogen. There are indications that rubber free from adsorbed oxygen would undergo no change on mechanical working in pure nitrogen.

3. The value of the so-called constant n in the plasticity equation $K = XY^n$ changes from one sample of masticated rubber to another. It varies from 0.07 in the case of a tough raw rubber full of nerve, to 0.28 in the case of the same rubber masticated in air or oxygen until thoroughly "killed."

4. Small quantities of ozone are formed by the static electrical charges produced on rubber during mastication.

5. Rubber does not masticate more rapidly in ozonized air or ozonized oxygen than in air and oxygen, respectively.

6. The volatile products of the action of ozone on vulcanized rubber have a retarding action on the mastication of rubber, particularly during the initial stages.
7. Dry rubber gains steadily in weight during mastication in air. The rate of absorption of oxygen decreases slightly until the rubber has gained 0.22 per cent in weight. Thereafter, the rubber becomes tacky and the rate of absorption increases.
8. During mastication of rubber in air or oxygen, volatile products are evolved having an acrid odor resembling that of the aldehydic products of the reaction between ozone and vulcanized rubber.
9. A suggested mechanism of mastication has been put forward to explain the above findings.

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Mastication of Rubber

An Oxidation Process

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CHANGES IN RUBBER which occur during mastication have been studied in an attempt to determine whether the breaking down of rubber by milling is a mechanical or a chemical process. Using the photographic-plate test, peroxides were detected in smoked sheets, both after milling and after exposure to light in the presence of oxygen, and the concentration was higher when the rubber was milled on cool rolls than when milled on hot rolls. Pale crepe did not give as strong a test for peroxides, while the peroxides could not be detected at all in fine Para and sprayed latex. These rubbers contain some material which can decompose hydrogen peroxide.

The softening of rubber on the mill is probably due to the breaking up of the long rubber molecules into shorter ones by an oxidation process. Oxidation occurs quite rapidly on the mill because the rubber molecules are activated by mechanical distortion, and the oxygen is activated by electrical charges. The stresses in the rubber and the electrical charges are both greater when milling is done on cool rolls than when done on hot rolls, which accounts for the greater effectiveness of cold-milling.

This theory was verified by the peroxide experiments, by milling peroxides into rubber, and by the

luminescence effects which were observed during milling. As a final check on the theory, rubber was milled in the presence of various gases. It was found that little, if any, breakdown of the rubber occurs if the milling is done in the absence of oxygen.

THE mechanism of the breakdown of rubber on the mill has been investigated by many workers, and many different theories have been advanced to explain the changes which occur. In some cases the theories have been based on a postulated structure of the latex particle, but, more often, they were *ad hoc* explanations based on the authors' pictures of the structure of the rubber molecule. Countless attempts have been made to distinguish between "depolymerization" and "disaggregation" of rubber molecules, where in many cases the difference is merely one of definition. Only recently have data become available to show that milling is not the simple mechanical process it once was thought to be, but is essentially a chemical reaction.

Previous Work

It is well known that the latex globules are broken up during milling (*8*, *9*, *10*), and Van Rossem (*27*), adopting Hauser's picture of the latex particle, claimed that the plasticizing effect of milling is due to the mixing of the soft inner phase with the hard outer phase of the globules. This does not explain why the plasticity of rubber continues to increase during milling, even when all the latex globules are broken up, nor does it agree with the results of Staudinger (*23*), which indicate that the molecular weight of milled rubber is considerably less than that of unmilled. Staudinger believes that the breakdown of rubber on the mill is a mechanical disruption of the primary valence bonds in the rubber molecules, such as occurs in crushing a diamond. Pummerer (*17*), on the other hand, claims that the molecular weight of rubber is low, and milling merely breaks up the micelles, which are large aggregates of molecules.

Bary and Hauser (*1*) have claimed that the softening of rubber by milling is due to a shifting of the equilibrium between two definite phases which they believe to exist in rubber; alpha-rubber, consisting of rubber hydrocarbon in a relatively low state of polymerization; and beta-rubber, having a higher degree of polymerization, presumably with little or none of the rubber in the intermediate states of polymerization. (It is unfortunate that the terms alpha- and beta-rubber have recently been used in this sense, in view of their previous use in the opposite sense by Pohle (*16*).) They claim that heat has the same effect as milling in shifting the equilibrium between these two phases. The apparently permanent effect of heat and milling is explained on this

theory by the slow speed of repolymerization resulting from the high viscosity of rubber. This view is not supported by the actual behavior of rubber.

Many early investigators suspected that oxygen played an important part in milling, but they could not prove it, and they finally concluded that the effect of oxygen was either negligible or deleterious. Fisher and Gray (*6*) found that rubber milled several hours in carbon dioxide became very soft and tacky, but the change in unsaturation could not be measured (i. e., was less than 0.5 per cent). Rubber milled several hours in air had its unsaturation lowered by about 2 per cent, which, they said, may have been due to oxidation or to the formation of a cyclo-rubber. Garner (*8*) claimed that milling first depolymerized or disaggregated the rubber hydrocarbon, after which it could react with oxygen to become tacky. Messenger (*14*) found that milling rubber changed its heat of combustion by less than 0.5 per cent, although the viscosity was changed by a factor of 20, which seemed to indicate the amount of oxidation which occurs during milling is negligible.

The view was further supported by the fact that rubber could be softened to some extent by heating in steam or carbon dioxide (*9, 15*), while heating for a long time in air totally ruined the rubber. The belief in the deleterious effect of oxygen led the Dunlop Rubber Company (*31*) to patent the method of softening rubber by heating it in an inert non-oxidizing atmosphere previous to milling. Staudinger (*22*) also patented the method of masticating rubber in an inert atmosphere to avoid the deleterious effects of oxygen.

Recently Fry and Porritt (*7*) showed that nearly all the permanent softening, which occurs in heating rubber in a supposedly inert atmosphere, actually is due to the traces of oxygen which are present, even 0.01 per cent of oxygen causing a very marked effect on rubber when it is heated for several hours at 150° C. From the similarity in the effects of heating and milling on the viscosity and plasticity of rubber, they suggest that the effect of milling may also be due to oxidation.

The very large effects produced by minute traces of oxygen are consistent with the views of Staudinger that rubber has a molecular weight of the order of 100,000. If one molecule of oxygen breaks a rubber molecule into two parts, only 0.03 per cent oxygen is necessary to reduce the molecular weight to 50,000. The combining of about 0.5 per cent oxygen reduces the average molecular weight of the rubber to about 5000. If one oxygen atom saturates each double bond, it takes only about 0.5 per cent oxygen to reduce the unsaturation by 2 per cent, the value found by Fisher and Gray.

In the light of these facts, the available experimental data are not sufficiently accurate to show whether or not the softening of rubber on milling is due to oxygen. Because of the inconclusive state of the problem, an attempt has been made to obtain additional evidence which might answer two ques-

tions: first, does oxidation occur during milling; and second, if oxidation does occur, is this essential to the breakdown of the rubber on the mill? In the first part of this work, several different lines of indirect evidence were obtained to throw light on these questions. The conclusions from the early work were then verified by milling rubber in the presence of various gases. The results of this work are in agreement with those of a similar test recently reported by Cotton (*2*).

If rubber is oxidized during milling, the first product formed probably is a peroxide, since most unsaturated compounds are oxidized through the formation of intermediate peroxides. One of the most sensitive, though unfortunately not a specific test for volatile peroxides, is the formation of latent images when they act on photographic plates (*13*). The action of hydrogen peroxide on a plate is similar in every respect to that of light (*21*). It is reported that the test is so sensitive that it can detect the peroxides formed when certain metals (zinc, aluminum, cadmium) are exposed to light in moist air, but no effect is produced when they are exposed to light in dry air (*5*, *13*, *19*). Russell (*18*) found that a large number of materials produced a latent image on a photographic plate in the dark if the material were previously exposed in air to light—a treatment which undoubtedly causes the formation of peroxides. This effect on the photographic plate has been used to study the formation of peroxides in drying oils (*24*), although the amounts of peroxide formed here are great enough after short exposure to be detected chemically (*25*). Van Rossem and Dekker (*28*) reported that rubber which had been exposed to the light could form a latent image if placed on a photographic plate in the dark, and they found the effect to be greater with smoked sheets than with pale crepe.

If peroxides are formed during milling, they might be detectable by this method. Negative results, of course, would be inconclusive, since, even though peroxides were formed during milling, they might not be volatile, or the surface concentration might not be great enough, or catalysts might be present which would destroy the peroxides before they could be detected. The following experiments show that peroxides are formed in rubber during milling just as on exposure to the light, but that they can be detected only in certain rubbers. Some rubbers contain catalysts which decompose peroxides, and these rubbers also exhibit the slowest plasticity changes during milling.

Formation of Peroxides in Rubber

Effect of Light. Samples of rubber were exposed for various times to a 220-volt printing arc, using National Carbon Company's Therapeutic "A" carbons, usually at a distance of 50 cm. from the arc. In every case a part of the sample was protected from the light by a strip of metal foil, leaving a control area of unexposed rubber on each sample. After exposure, the strips of metal were removed, and the

exposed side of the rubber samples put directly on the emulsion of a photographic plate where they usually were allowed to remain in the dark for about 18 to 24 hours, after which the plate was developed.

The first attempts to duplicate the work of Van Rossem and Dekker failed, because ordinary process or panchromatic plates were used. When Eastman "Speedway" or Gavaert "Super Sensima" plates were used, however, samples of smoked sheet produced a very strong image after less than a 1-minute exposure to the arc, and these plates were used in all subsequent work. It is known that the sensitivity of different plates to hydrogen peroxide varies enormously just as does their sensitivity to light (*30*).

To show that the formation of the latent image was due to oxygen, the following experiment was performed:

Strips of crude smoked sheet were placed in Pyrex test tubes, through which air, carbon dioxide, and hydrogen, respectively, were allowed to flow for about 6 hours. Another test tube containing a strip of smoked sheet was evacuated to a pressure of 3.10^{-4} mm. of mercury for the same time, giving the air present in the sample a chance to diffuse out. The evacuated test tube was then sealed off, and the others were closed with clamps to exclude the air. The hydrogen and carbon dioxide, which were taken directly from commercial supply tanks, undoubtedly contained traces of oxygen as an impurity. Two of the tubes were filled with hydrogen and from one the stopper was partially removed for a fraction of a second to admit a small amount of air. The samples were given a relatively long exposure (10 minutes) to the arc light while surrounded by these gases, and another sample of smoked sheet was exposed directly to the light without being shielded by glass.

The results are shown in Figure 1. It is seen that the sample exposed in the evacuated tube produced only a barely detectable image. The samples exposed in hydrogen and carbon dioxide formed considerably stronger images, though they were still much weaker than the image formed by the sample exposed in contact with an appreciable amount of air. The dark band across each sample shows where the rubber was protected from the light by the metal strip. It is difficult to say whether the images formed after exposure in hydrogen and carbon dioxide are due to oxygen present as an impurity in the gas or to oxygen originally present in the sample, although the former is more probable. The results show that extreme ultra-violet light is not necessary to produce this effect, since the activating rays passed through the glass.

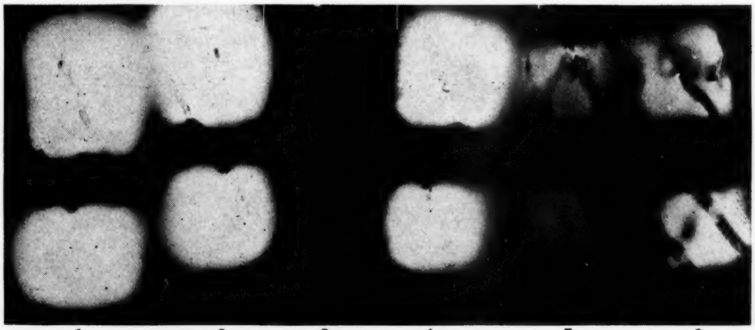
The formation of the latent image is not due to a luminescence or phosphorescence of the rubber, since no image is formed if the rubber is separated from the photographic emulsion by a microscope cover-glass, or even a thin (0.0010-inch) sheet of cellophane, but the active material can travel through a few millimeters of air and still affect the plate. This material is undoubtedly a volatile peroxide, possibly hydrogen peroxide which splits off from the oxidized rubber.

In the rest of the report this volatile material will be referred to as hydrogen peroxide.

EFFECT OF MILLING. To determine if milling would also produce this peroxide in smoked sheet, one sample was milled 4 minutes on a cold 4 × 4 inch mill, while another was milled the same length of time with steam-heated rolls. A third sample was dead-milled and then allowed to stand 3 days before being put on the photographic plate. Other samples of crude smoked sheet were exposed to light and then were placed with the milled samples on the photographic plate.

The results, shown in Figure 2, indicate that not only is the peroxide formed during milling, but that its effective concentration is higher after cold-milling (sample 2) than after hot-milling (sample 3), and that some of the peroxide remains in the rubber for at least 3 days after milling (sample 4).

The difference in the results after hot- and cold-milling



1 2 3 4 5 6

FIGURE 1. IMAGES FORMED BY SMOKED SHEET WHEN EXPOSED TO ARC LIGHT IN DIFFERENT GASES

(All except No. 1 exposed in Pyrex test tubes)

1. Air
2. Air
3. Vacuum (3.10^{-4} mm. Hg)
4. Hydrogen containing air
5. Hydrogen
6. Carbon dioxide

may be attributed to the fact that cold-milling is more effective than hot-milling in forming the peroxide, and to a more rapid decomposition of the peroxide at high temperatures. The evidence that the formation of the peroxide is more rapid at the lower temperature suggests that this phenomenon is fundamentally related to the breakdown of the rubber.

The stability of the peroxide was tested by storing samples treated the same as those in Figure 2 for 18 days, and then putting them on a photographic plate. The samples which were milled cold or exposed to light for long periods still produced faint but definite images after this time. It is possible that none of the original peroxide formed by the light or milling remained after 18 days, but that the decomposition of the original peroxide started reaction chains, resulting in the formation of more rubber peroxide.

Heating a sample of smoked sheet for 5 minutes at 200° C.

in unpurified carbon dioxide, after it had been exposed to the light, weakened but did not destroy its ability to affect a photographic plate; after heating for 15 minutes under these conditions, the rubber still had a slight but definite effect on a plate. Heating smoked sheet in air at this temperature caused it to become so tacky that it could scarcely be removed from photographic plate after resting on it overnight. There was some evidence, however, of the formation of a very weak latent image.

Results with Different Rubbers. The formation of peroxide by light and milling was studied for several different rubbers. It was found that they produced images of widely different intensities, but it was particularly noted that the order of intensity for different rubbers was always the same, whether the peroxide was formed by exposure to light or by milling. Smoked sheet and balata formed the strongest images, while pale crepe always produced a considerably weaker image, and none at all was obtained from No. 1 sprayed latex, fine Para, or guayule. That the rate of change of plasticity with time of milling for different rubbers increases in the order—sprayed latex, pale crepe, smoked sheet (*4*)—seems to signify that the peroxide formation and change in plasticity are quantitatively related.

The negative results for sprayed latex and fine Para probably are not due to any lack of formation of peroxide, but to the fact that the peroxide is decomposed by some material present in these rubbers soon after it is formed. This is shown by the fact that a 50:50, or even in some cases a 25:75, mixture of sprayed latex and smoked sheets will not produce any latent image after being milled or exposed to light, or after both treatments.

This view was confirmed by tests in which hydrogen peroxide was milled into sprayed latex, Para, and smoked sheet. When the samples were put on a photographic plate within an hour after milling, each of them formed a very strong image. However, if the batches were allowed to stand for 24 hours, and the samples then put on photographic plates, the image formed by smoked sheet was almost as strong as before; but the sprayed latex and Para formed no image, showing that during this period they had decomposed the peroxide which had been added.

Several unsuccessful attempts were made to remove from the rubber the material that destroyed the peroxide. Soaking thin strips of sprayed latex in running warm water, in acetone, or in alcohol for periods up to 11 days, followed by drying for about 8 hours, was not effective; nor did drying a sample over sulfuric acid for 11 days before exposing to light render it active toward a photographic plate. Smoked sheet was not affected by drying, but soaking it in acetone or alcohol for 11 days greatly reduced its power to form a latent image after exposure to the light. After soaking the smoked sheet in water for 11 days and drying in air for 8 hours, it did not have

the power to form a latent image, though the soaking in water caused the sample to become very tacky.

An uncured smoked sheet-sulfur mixture produced an image after exposure to the light, but with progressively longer cures the ability to form a latent image was gradually reduced, and the fully cured and overcured samples did not form an image under any conditions. This may have been due to the decomposition of the peroxide by traces of hydrogen sulfide formed during cure. It is also possible that vulcanized rubber itself reacts more readily than unvulcanized rubber with the peroxide.

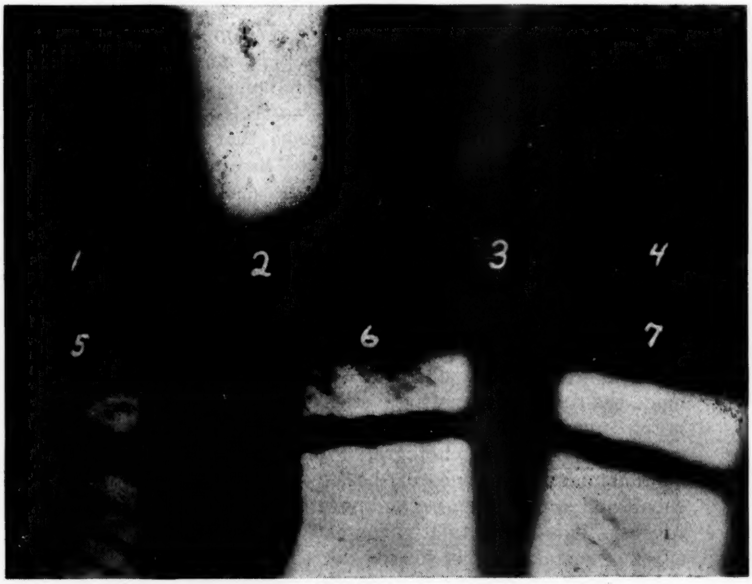


FIGURE 2. PEROXIDE FORMATION BY LIGHT AND MILLING

1. Control (untreated)
2. Milled 4 minutes on cold mill
3. Milled 4 minutes on mill
4. Dead-milled and stored 3 days
5. Exposed to arc light 30 seconds at 25 cm.
6. Exposed to arc light 30 minutes at 25 cm.
7. Exposed to arc light 30 minutes at 60 cm.

EFFECT OF VARIOUS CHEMICALS. It was thought at one time that this phenomenon might offer a good general method of testing antioxidants. This did not prove to be the case, for most age-resisters, because of their amine content, affected the plate without being exposed to the light. However, several interesting results were obtained in the presence of metal soaps. Stearates of copper, cobalt, manganese, and zinc, and linoleates of copper and cobalt were used, milling 3 per cent of each into smoked sheet.

When samples of these stocks, and of the controls milled without the addition of any metal soap, were placed on a photographic plate immediately after milling, moderately

strong images were formed by the controls and by the stocks containing zinc and manganese stearates, but no images were formed by the stocks containing copper and cobalt soaps. After two or three days the peroxides formed during milling could no longer be detected in any of the stocks. Samples of each stock were then exposed to the arc light and again tested for peroxides. The order of intensity of the images was the same as found immediately after milling. The copper and cobalt soaps destroyed the peroxides formed by the light, so that these stocks produced no images; from the stocks containing zinc and manganese soaps and from the controls, dense images on the photographic plate were obtained. Similar results were obtained after the stocks had stood for various times up to a month, except for the sample containing cobalt linoleate. At the end of a week this sample produced no image on a photographic plate before being exposed to the light, but, after exposing the sample to the arc light for 30 minutes, it formed a very dense image that extended for several centimeters from the sample. The samples containing cobalt stearate and both of the copper soaps produced no image whatsoever after this treatment. Two weeks after the cobalt linoleate was added to the rubber, it had accelerated the oxidation so much that it caused this stock to give a very dense image on the photographic plate, even without exposing the rubber to the light. Neither cobalt stearate nor either of the copper soaps had this effect, even after the samples had stood for a month. Copper linoleate made the rubber very soft and sticky, but this oxidation was not accompanied by an evolution of hydrogen peroxide which could be detected on a photographic plate. There seems to be a fundamental difference in the effects of both copper and cobalt and of the saturated and unsaturated acid soaps in the rubber. It is interesting to compare these results with the effect of metal soaps in linseed oil. The addition of driers (lead, cobalt, and manganese soaps) reduces the amount of hydrogen peroxide given off; the addition of soaps of zinc, cadmium, or aluminum, which are not driers, enormously increases the amount of hydrogen peroxide liberated by the drying oil film (*24*).

Attempts to Develop Chemical Tests for Peroxides. Although it is very improbable that the above results could be due to anything but peroxides, or at least to some form of active oxygen, an attempt was made to obtain confirmatory chemical tests for peroxides. However, these were not successful except in the case of the sample containing copper linoleate which gave off large quantities of hydrogen peroxide. On making an aqueous extract of smoked sheet, or even rinsing the surface of smoked sheets a few times, a solution is obtained which will reduce either ferric chloride or free iodine; thus the usual tests for peroxides, such as the titanium sulfate, chromic acid or starch–potassium iodide tests, are useless to detect the small amounts of peroxides formed by light or

milling. There are more water-soluble reducing materials present in smoked sheets than are required to decompose any peroxides that may be present, so that the peroxides are reduced as soon as the surface is wet. This also explains why the sample of smoked sheet soaked in water for 11 days could not form any image on the photographic plate.

A few attempts were made to obtain solutions of the peroxides in various solvents, such as chloroform, carbon tetrachloride, etc., by washing with these solvents the surface of samples that had been milled or had been exposed to light, but in no case was a satisfactory test obtained. No peroxide could be detected in air which flowed past a sample of smoked sheet in a Pyrex test tube during exposure of several hours to the arc light. Undoubtedly with sufficient time and patience a chemical test could be obtained, but this was not considered necessary in view of the evidence later obtained which conclusively showed the importance of oxygen during milling.

Mechanism of Oxidation on the Mill

The above experiments show that rubber is oxidized at a fairly rapid rate during milling in air, and they raise the question as to how this oxidation is brought about. Rapid oxidation is probably caused by two factors: the increase in the potential energy of the long rubber molecules, due to mechanical deformation which makes them more reactive; and the activation of the oxygen by the electric charge developed by the rubber.

It is well known that vulcanized rubber is much more reactive to ozone and oxygen when slightly stretched than when unstretched (*11*), and this is also true for unvulcanized rubber. The stretching of rubber causes a distortion of the molecules, increasing their internal energy just as straining increases the single electrode potential of metals and their reactivity toward oxygen (*26*). This factor is probably more effective whenever the molecules are larger, and thus the larger molecules are broken down first.

The rate of oxidation is also increased by the activation of oxygen during milling, owing to the electric charge which develops. It has been shown (*3*) that, in the presence of moisture, oxygen has a strong affinity for electrons, forming ion clusters. Since the rubber acquires a charge on going through the mill, the oxygen probably tends to form ion clusters on the surface of the rubber, which could easily cause the formation of a rubber peroxide.

The charge on the rubber may reach a potential sufficiently high not only to form ion clusters on the surface of the rubber, but also to form ionized oxygen molecules, O_2^- and O_2^+, and even ionized oxygen atoms and ozone. In these cases the oxygen would be even more strongly activated than when it was in the form of ion clusters; and it probably would combine with the strained rubber more readily, although this extreme activation probably is not necessary to cause the reaction.

With these conditions during milling, it would be surprising not to have the rubber molecules oxidized, in fact it would be almost impossible to prevent it. The term "molecule" is used here in the sense of the mechanical molecule or group of atoms which stay together when the rubber flows under a shearing stress, since the mechanical properties of the milled rubber are the ones which are most interesting for the purposes of these experiments. This term will be discussed more fully elsewhere. However, the evidence strongly suggests that the chemical and mechanical molecules of rubber are the same.

It does not follow from this theory that antioxidants will necessarily prevent the softening of rubber on the mill, although it would be expected that part of the antioxidants would be oxidized. Overmilled stocks have notoriously bad aging properties (*29*), probably owing to the oxidation of the natural and added age-resisters. It is well known that most of the chemical antioxidants are not effective against sunlight or ozone aging, where rubber is attacked by activated oxygen, and good age-resisters may also be ineffective in preventing the activated rubber from being attacked by activated oxygen on the mill.

Confirmatory Evidence for the Proposed Theory of Milling

Electrical Effects. The importance of the electrical effects in the breakdown of rubber during milling as postulated above is supported by some rather interesting observations on the accompanying luminescence effects. When rubber is milled on a 4 × 4 inch mill with cold rolls, no electrical discharge takes place underneath the bite, as might be expected, but there is a more or less even glow over the surface of the rubber for about 1 or 2 cm. where the rubber enters the bank, and occasionally tiny sparks can be seen jumping from the blanket to the bank. In fact, most of the frying and crackling noise that is heard on a small mill, which is often attributed to the bursting of small air bubbles, is due to these sparks. This effect can be observed with gas-black mixtures as well as with pure gum stocks and with dead-milled, as well as slightly milled rubber, providing the rolls are cold. However, if the rolls are heated, this effect disappears, but it reappears on cooling the rolls. This shows a striking correlation with the smaller yield of peroxide which was observed on hot-milling, and with the fact that the rate of breakdown of rubber is greater when the rolls are cool than when they are hot.

Addition of Peroxides to Rubber on the Mill. If the breakdown of rubber on the mill is a chemical reaction involving activated oxygen, one might expect the reaction to go faster if a peroxide were added to the rubber on the mill. It was found that the addition of 5 cc. of hydrogen peroxide to 300-gram batches of smoked sheets increased the plasticity, as shown in Table I. All plasticity measurements reported in

this paper are made at 100° C. with the Goodrich plastometer (*12*).

TABLE I. EFFECT OF ADDING PEROXIDE TO RUBBER ON THE MILL

MILLING TIME	MATERIAL ADDED	PLASTICITY AFTER MILLING
Minutes	*5 Cc.*	
6	Water	11.4
6	Peroxide	13.9
10	Water	46.0
10	Peroxide	70.4

The addition of larger amounts of peroxide had a greater effect. As would be expected from the photographic tests, the addition of 5 cc. of hydrogen peroxide to a 300-gram batch of sprayed latex had less effect on the plasticity.

MASTICATION OF RUBBER IN PRESENCE OF VARIOUS GASES. As a final check on the theory, samples of rubber were milled in a Day internal mixer fitted with an air-tight cover, through which various gases could be passed. Rubber in 500-gram batches was milled 20 minutes, using Banbury-type blades in the mixer. Prime smoked sheets were milled in air, oxygen, and hydrogen. Hard sprayed latex was also tested, since it acted very differently from smoked sheets in the photographic peroxide tests. It was milled in air, oxygen, hydrogen, nitrogen, and carbon dioxide. No attempt was made to remove the air from the rubber, and the gases other than air were used directly from the cylinder without any purification. It was expected that there would be enough oxygen in the rubber and the gases to produce some softening, but it was anticipated that the amount of softening due to these traces of oxygen would be small.

Two or three batches of each rubber were masticated in oxygen and hydrogen, and single batches in the other gases. The different gases were used in random order, and, to prevent any gradual changes in temperature or other conditions from introducing systematic errors, the duplicate batches with the same gas were never run consecutively. Duplicate plasticity determinations were made on each batch. The average plasticity of all samples of each rubber was determined, as well as the average deviation of the single plasticity measurements. Table II shows the results obtained.

TABLE II. PLASTICITY OF RUBBER MILLED IN VARIOUS GASES

GAS	SMOKED SHEETS Batches	Plasticity	SPRAYED LATEX Batches	Plasticity
Unmilled	.	4.5 ± 0.2	.	1.5
Oxygen	2	18.9 ± 0.8	2	6.6 ± 0.6
Air	1	22.1 ± 0.4	1	9.0 ± 0.6
Hydrogen	2	5.9 ± 0.6	3	2.9 ± 0.5
Nitrogen	.	.....	1	1.8 ± 0.1
Carbon dioxide	.	.....	1	2.5 ± 0.1

The data show conclusively that the major part of the breakdown of smoked sheets in the internal mixer is not due to a mechanical breaking up of the molecules (as suggested by Staudinger) or to a mechanical breakdown of micelles or

aggregates (as is commonly believed) but to an oxidation process; and the same conclusion should hold for smoked sheets broken down on the mill. Since the sensitivity of the plastometer is not very great at the lower end of the scale, the data for sprayed latex are more scattered, but they indicate that at least the major part of the breakdown which occurs when this rubber is milled is due to an oxidation process. The single batches milled in air had higher plasticities than those milled in oxygen, but the difference is not significant. It may have been due to slight temperature changes during the mastication or to a variation in the original rubbers. Later experiments indicate that milling in oxygen is as effective as milling in air.

To make a more drastic test of the theory, a few batches were milled in purified hydrogen and nitrogen for periods of 2 and 4 hours in the same mixer used for the above tests. To reduce the amount of oxygen dissolved in the rubber, the samples were kept in an atmosphere of nitrogen for from 2 to 4 days before the tests, and they were exposed to the air for as short a time as possible when they were transferred to the mixer. The nitrogen was purified by bubbling through alkaline pyrogallol, and the hydrogen was purified by passing over hot platinized asbestos. The results of these tests and of one experiment in which rubber was milled in oxygen are shown in Table III.

TABLE III. EFFECT OF MILLING FOR LONG TIMES IN PURIFIED GASES

Kind of Rubber	Gas Used in Milling	Time of Milling	Plasticity Before milling	Plasticity After milling
		Hours		
Smoked sheets	Oxygen	2	3.3	64.6
Smoked sheets	Hydrogen	2	3.0	6.6
Smoked sheets	Hydrogen	4	3.1	6.1
Smoked sheets	Nitrogen	2	2.8	6.3
Sprayed latex	Nitrogen	2	2.1	3.1

Even these long times of milling did not greatly change the plasticity of the samples if oxygen was excluded, but milling the rubber in oxygen made it very plastic.

When acetone-extracted rubber was used, the effect of oxygen in milling was even more striking. A sample of extracted smoked sheet, having a plasticity of 7.0, was milled in oxygen for 20 minutes, after which its plasticity was 58.9; another sample milled in nitrogen for the same time had a plasticity of only 9.5.

Shacklock (*20*) recently measured the surface tension of solutions of rubber broken down in various ways, in an attempt to distinguish between a depolymerization and a disaggregation of the rubber. It would be very surprising if a straight depolymerization of the rubber would have much effect on the surface tension of a benzene solution, for most hydrocarbons with a density around 0.9 have a surface tension very close to that of benzene. Hence the small amount of

depolymerization necessary to account for the change in physical properties would not be expected to change the surface tension of the solution. However, if rubber were broken down through an oxidation process, the oxidation product, whether a peroxide, acid, aldehyde, or alcohol, might be different enough chemically from the hydrocarbon to have an appreciable effect on the surface tension. Shacklock's results show that the cold-milling of rubber had more effect on the surface tension of the solutions than any other treatment, and hot-milling came next; but heating the rubber or exposing the solution to ultra-violet light had no effect. This is consistent with the view that the compounds formed in the rubber during milling are more polar (perhaps because there are more peroxides) than the compounds formed on heating the rubber or exposing the solution to light.

Since this paper was first submitted, the report of Cotton (*2*) on the mastication of rubber in the absence of oxygen was received. He found that milling in an atmosphere of nitrogen was much less effective than milling in oxygen, as was found in the work reported above. Both Cotton and Shacklock emphasize the effects of ozone and ionized oxygen in breaking down the rubber, and they imply that the mechanical action which occurs on milling is important chiefly because it causes the formation of ozone and ionized oxygen. They do not recognize so clearly the importance of the mechanical distortion in activating the rubber molecules, but in other respects their views are similar to those presented above.

Summary

The effects of milling and of exposure to light are similar in altering smoked sheet, pale crepe, and balata so that they affect a photographic plate in the dark. This effect is due to the formation of a volatile peroxide, probably hydrogen peroxide. No image is formed by sprayed latex, fine Para, anode rubber, or guayule after being milled or exposed to the light.

The order of the intensity of the images formed by smoked sheets, pale crepe, and sprayed latex is the same as the order of their rate of change of plasticity on milling. Cold-milling is more effective than hot-milling, both in the formation of the peroxide and the breakdown of the rubber. Milling on a cold mill produces a luminous discharge from the blanket to the bank, but this disappears when the rolls are heated.

Sprayed latex and fine Para contain some material which decomposes hydrogen peroxide. This accounts for the fact that peroxides could not be detected in these rubbers, either after exposure to light or after milling, even with the addition of hydrogen peroxide. Both copper and cobalt soaps decompose the peroxide in some instances, though under other conditions the cobalt soaps greatly increase the amount of peroxide in the rubber.

A chemical reaction between rubber (activated through the

mechanical deformation) and oxygen (activated by electrical charges) is advanced as a theory to account for the formation of peroxides and for most of the breakdown of rubber during milling.

The theory is supported by the peroxide tests, by the luminescence effects on milling, and by the fact that the mechanical working of rubber produces, at the most, only a small change in plasticity if the rubber is worked in the absence of oxygen.

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Impure Iron Oxide as a Rubber Pigment

I. Effect of Ferric Sulfate on Cure and Aging of Rubber

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The traces of free ferric sulfate present in oxide of iron are shown by experiment to cause accelerated aging of rubber. This impurity markedly retards the rate of cure. Oxide of iron, treated with sodium carbonate in solution to change the soluble ferric sulfate to insoluble ferric carbonate, shows good aging properties and a high rate of cure. Aggregates of oxide of iron caused by ferric sulfate during its manufacture increase in frequency and size, and the color value of the pigment decreases as the percentage of retained ferric salt increases.

COMMERCIAL ferric oxide, commonly used as a coloring agent of red, tan, and brown rubber stock, invariably contains a small percentage of soluble ferric sulfate. The amount present varies from 0.005 to 4 per cent, depending upon the method used in the manufacture of the ferric oxide.

MANUFACTURE OF IRON OXIDE

Crystal ferrous sulfate, reclaimed from waste-steel pickling liquors, is oxidized in rotary kilns. Oxidation reactions which take place in the kiln are not completely understood, but it is supposed that part of the ferrous sulfate is first converted to the basic sulfate and then to ferric oxide with the formation of sulfur trioxide and sulfur dioxide. Some of the undecomposed ferrous sulfate is then oxidized by the sulfur trioxide and oxygen to ferric sulfate, which is then converted to ferric oxide and sulfur trioxide.

Complete conversion of the ferric sulfate to the ferric oxide is not commercially possible without harmfully affecting the

TABLE I. EFFECT OF FERRIC SULFATE IN BOMB AGING TESTS (SERIES I)

Ferric Sulfate	Before Aging		Elongation	After Aging 24 Hours		Elongation	After Aging 48 Hours		Elongation	After Aging 72 Hours		Elongation
%	Kg./cm.^{2}	(Lb./in.^{2})	%	Kg./cm.^{2}	(Lb./in.^{2})	%	Kg./cm.^{2}	(Lb./in.^{2})	%	Kg./cm.^{2}	(Lb./in.^{2})	%
Normal	206	(3075)	770	224	(3282)	730	231	(3278)	667	206	(2930)	650
0.50	201	(2885)	765	249	(3535)	706	220	(3120)	636	250	(3550)	653
1.00	209	(2970)	718	250	(3547)	686	249	(3540)	636	243	(3460)	580
2.50	197	(2800)	751	199	(2820)	686	236	(3355)	673	240	(3410)	646
6.00	158	(2250)	686	203	(2885)	630	215	(3055)	640	208	(2950)	636

TABLE II. EFFECT OF SODIUM CARBONATE IN BOMB AGING TESTS (SERIES I)

Sodium Carbonate	Before Aging		Elongation	After Aging 24 Hours		Elongation	After Aging 48 Hours		Elongation	After Aging 72 Hours		Elongation
%	Kg./cm.^{2}	(Lb./in.^{2})	%	Kg./cm.^{2}	(Lb./in.^{2})	%	Kg./cm.^{2}	(Lb./in.^{2})	%	Kg./cm.^{2}	(Lb./in.^{2})	%
0.03	205	(2910)	770	254	(3730)	740	254	(3610)	683	278	(3955)	683
0.10	205	(2910)	750	257	(3650)	736	268	(3810)	693	270	(3835)	683
0.60	221	(3143)	755	244	(3475)	743	265	(3760)	686	275	(3900)	683
2.00	210	(2980)	778	252	(3580)	713	262	(3715)	680	267	(3790)	653

color and brilliance of the pigment. After calcination, the remaining soluble salts are removed by decantation with water. Part of the ferric sulfate is adsorbed by the ferric oxide, and great difficulties are encountered in washing out the last traces of this salt.

The detrimental effects of ferric sulfate are overcome by treating the oxide with sodium carbonate as shown in the following experiments.

Methods of Test

All compounds were milled on a Farrell-Birmingham laboratory experimental mill. Care was taken that each batch was

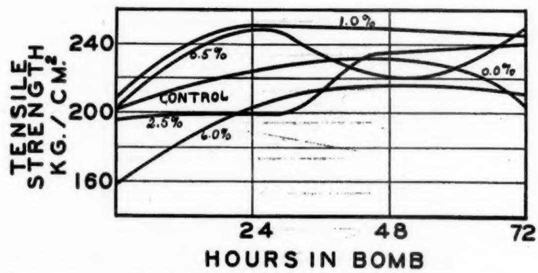

Figure 1. Effect of Increasing Percentages of Ferric Sulfate (Series I)

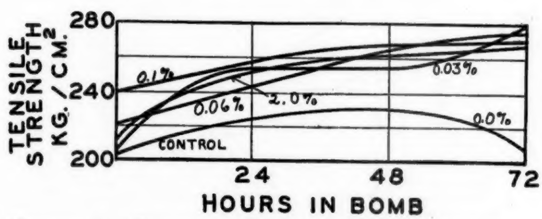

Figure 2. Effect of Increasing Percentages of Sodium Carbonate (Series I)

milled for exactly the same length of time and also cut back the same number of times on the rolls.

Master batches of all compounds were first milled, to which the color and accelerator were added just previous to cure.

A standard 6 × 6 inch four-cavity mold was used in curing the test slabs. An insulated press with cast-iron platens with automatic recording temperature and pressure gages was used, the surface of the platens having previously been tested for uniform heat transfer with a thermocouple.

All cured slabs were kept at an even temperature and humidity for 24 hours before breaking on a Scott testing machine. The elongation was taken visually from a measuring tape, the rate of elongation being 20 inches (50.8 cm.) per minute.

Aging Tests. Uniform oxygen pressure 300 pounds per square inch (21.1 kg. per sq. cm.) was supplied from an oxygen cylinder to a standard Bierer-Davis bomb, completely submerged in a thermostatically controlled circulating water bath at 60° C.

Circulating air was supplied to a standard Geer oven by an electric fan, the oven being electrically heated to 70° C. and thermostatically controlled.

Control Tests. Cure curves were run on all compounds used in this work to determine the optimum point of each. The hand-tear test was not applied. Curing times sufficient to bring the stock to the point just below the optimum were chosen.

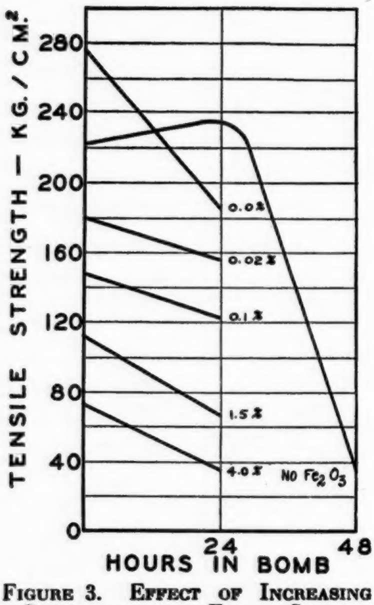

Figure 3. Effect of Increasing Percentages of Ferric Sulfate (Series II)

The aging tests were grouped into two series—namely, the sulfate series and the carbonate series.

The control samples were run through the laboratory at the same time as the prepared samples so that all associated test batches were subjected to the same conditions.

A standard red oxide of iron of the following analysis was chosen for the experiments:

	%		%
Oxide of iron	99.15	Manganese	0.0227
Silicon dioxide	0.29	Calcium oxide	0.146
Alumina	0.10	Magnesium oxide	0.02
Total soluble sulfates[a]	0.13	Water	0.28
Copper	0.0042		

[a] Includes salts of magnesium and calcium from wash water.

Series I

The following standard blanc-fixé red oxide of iron tube compound was chosen for the first series of experiments:

	Grams		Grams
Pale crepe	66.00	Stearic acid	0.50
Zinc oxide	3.50	Sulfur	1.625
Lithopone	3.00	Captax	0.75
Blanc fixé	24.00	Oxide of iron	2.00

Cure, 8 minutes: 4.2 kg. per sq. cm. (60 lb. per sq. in.).

The use of Captax as an accelerator might be criticized because of its good aging characteristics which might offset any

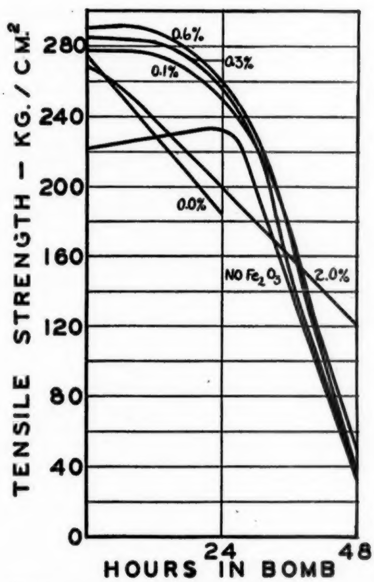

Figure 4. Effect of Increasing Percentages of Sodium Carbonate (Series II)

slight deteriorating effect of the ferric sulfate present in the oxide of iron. This compound represents plant practices and was chosen for this reason.

Bomb aging tests were run on the above compound at 60° C. and 21.1 kg. per square centimeter (300 pounds per square inch). The results are shown in Table I and Figure 1.

Four samples of oxide of iron were treated with solutions of increasing concentrations of ferric sulfate, after which they were dried, repulverized, and compounded into the above tube stock. The amount of ferric sulfate present in each oxide, as indicated in Table I, was calculated on the weight of the oxide of iron present in the compound, and includes the amount of ferric sulfate present in the oxide of iron as shown in the analysis above.

Sample 4 containing 6 per cent ferric sulfate, calculated on the weight of the oxide of iron, equal to 0.1 per cent of the total weight of the compound or 0.18 per cent of the weight of the rubber present, caused a marked retardation of cure and also a decrease in tensile properties after 72 hours of bomb aging.

The same oxide of iron was treated with solutions of sodium carbonate of varying concentrations, after which they were washed, dried, repulverized, and incorporated in the tube compound. In this manner the soluble ferric sulfate was converted to insoluble ferric carbonate. The percentage of sodium carbonate in the prepared samples is the analyzed alkalinity of each. Excess sodium carbonate is unquestion-

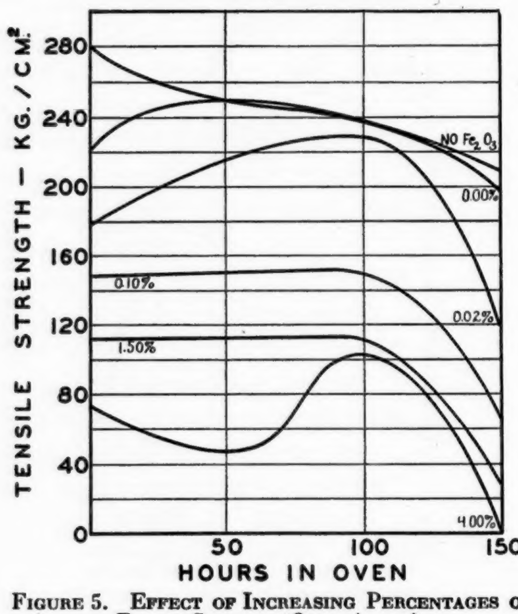

FIGURE 5. EFFECT OF INCREASING PERCENTAGES OF FERRIC SULFATE (OVEN AGING)

ably responsible for some of the accelerated cure shown in the data. High percentages of sodium carbonate were used in samples 3 and 4 to determine the effect of a large excess of this material.

These four samples were bomb aged, the results of which are shown in Table II and Figure 2.

The results show an acceleration of cure and an average tensile strength of 19 kg. per square centimeter (270 pounds per square inch) higher than the same oxide containing only traces of ferric sulfate.

The oxide treated with sodium carbonate moved towards the stress axis of the stress-strain curve as indicated by the comparative elongation figures in Tables I and II.

Series II

A second series of tests was run, using a standard D. P. G. test compound having poor aging characteristics to exaggerate the deteriorating properties of ferric sulfate:

	Grams
Rubber	100.00
Zinc oxide	5.00
Sulfur	4.00
D. P. G.	0.75
Oxide of iron	25.00

Cure, 60 minutes: 2.7 kg. per sq. cm. (38 lb. per sq. in.).

This compound was first bomb aged, leaving out all oxide of iron. No attempt was made to substitute another filler for the oxide.

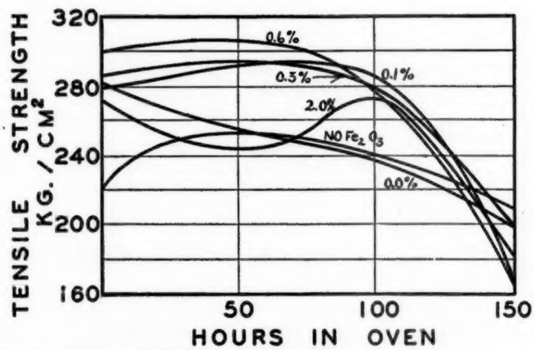

Figure 6. Effect of Increasing Percentages of Sodium Carbonate (Oven Aging)

Table III. Effect of Ferric Sulfates in Bomb Aging Tests (Series II)

Ferric Sulfate	Before Aging		Elongation	After Aging 24 Hours		Elongation	After Aging 48 Hours		Elongation
%	Kg./cm.²	(Lb./in.²)	%	Kg./cm.²	(Lb./in.²)	%	Kg./cm.²	(Lb./in.²)	%
No ferric oxide	322	(3154)	755	235	(3340)	765	33	(430)	450
Ferric oxide compound	278	(3995)	720	185	(2635)	700	..	...	...
0.02	179	(2535)	665	156	(2213)	660	..	...	...
0.10	148	(2100)	675	122	(1735)	665	..	...	...
1.50	112	(1590)	700	67	(950)	615	..	...	...
4.00	73	(1035)	715	36	(510)	670	..	...	...

Table IV. Effect of Sodium Carbonate in Bomb Aging Tests (Series II)

Sodium Carbonate	Before Aging		Elongation	After Aging 24 Hours		Elongation	After Aging 48 Hours		Elongation
%	Kg./cm.²	(Lb./in.²)	%	Kg./cm.²	(Lb./in.²)	%	Kg./cm.²	(Lb./in.²)	%
0.03	285	(4055)	712	256	(3630)	705	32	(430)	295
0.10	278	(3950)	705	250	(3555)	695	50	(720)	395
0.60	290	(4255)	697	262	(3720)	675	36	(510)	280
2.00	271	(3850)	615	200	(2850)	585	121	(1720)	490

TABLE V. EFFECT OF FERRIC SULFATE IN OVEN AGING TESTS

Ferric Sulfate	Before Aging		Elongation	After Aging 50 Hours		Elongation	After Aging 100 Hours		Elongation	After Aging 150 Hours		Elongation
%	*Kg./cm.*[2]	(*Lb./in.*[2])	%	*Kg./cm.*[2]	(*Lb./in.*[2])	%	*Kg./cm.*[2]	(*Lb./in.*[2])	%	*Kg./cm.*[2]	(*Lb./in.*[2])	%
No ferric oxide	221	(3145)	755	254	(3615)	715	240	(3540)	675	210	(2980)	625
Ferric oxide compound	280	(3995)	720	256	(3640)	730	238	(3770)	740	198	(2810)	710
0.02	178	(2535)	665	214	(3045)	685	229	(3230)	670	121	(1715)	620
0.10	148	(2100)	675	151	(2145)	665	150	(2140)	640	69	(980)	565
1.50	112	(1590)	700	113	(1600)	685	112	(1590)	660	27	(386)	520
4.00	73	(1035)	715	45	(640)	540	105	(1500)	570	2.6	(37)	385

TABLE VI. EFFECT OF SODIUM CARBONATE IN OVEN AGING TESTS

Sodium Carbonate	Before Aging		Elongation	After Aging 50 Hours		Elongation	After Aging 100 Hours		Elongation	After Aging 150 Hours		Elongation
%	*Kg./cm.*[2]	(*Lb./in.*[2])	%	*Kg./cm.*[2]	(*Lb./in.*[2])	%	*Kg./cm.*[2]	(*Lb./in.*[2])	%	*Kg./cm.*[2]	(*Lb./in.*[2])	%
0.03	286	(4055)	712	294	(4040)	735	278	(3950)	630	198	(2810)	660
0.10	378	(3950)	705	291	(4125)	697	286	(4050)	675	166	(2360)	610
0.60	300	(4255)	697	301	(4280)	680	276	(3925)	640	165	(2350)	575
2.00	271	(3850)	615	242	(3440)	620	273	(3880)	680	183	(2600)	530

Four samples of oxide were treated with ferric sulfate and four with sodium carbonate as in series I. The amount of ferric sulfate present in each oxide sample as indicated in Table III was calculated on the weight of the oxide of iron present in the compound and includes the amount of ferric sulfate present in the oxide of iron as shown in the analysis above.

The percentage of sodium carbonate in the prepared samples is the analyzed alkalinity of each.

Each sample was incorporated in the test compound and bomb aged. The results are shown in Tables III and IV and Figures 3 and 4.

The results show marked retardation of cure and accelerated aging with increasing percentages of ferric sulfate. The oxide of iron treated with sodium carbonate is similar in age resistance to the stock containing no oxide of iron, and the acceleration of cure was very apparent after 72 hours in the bomb.

The same tests were repeated in the Geer oven at 70° C. for 50, 100, and 150 hours. The results are shown in Tables V and VI, and closely parallel the bomb tests.

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II. Cause of Aggregation and Poor Dispersion of Oxide of Iron in Rubber

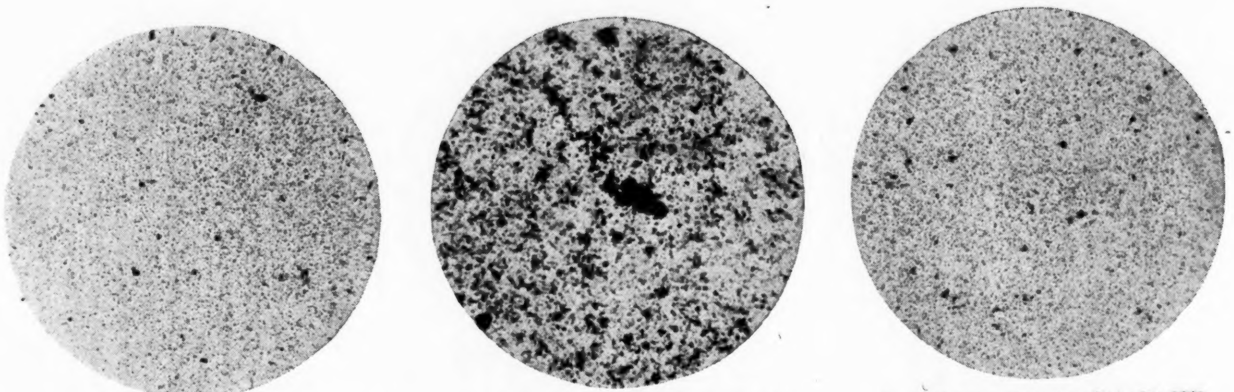
FINELY divided oxide of iron suspended in water is very sensitive to the pH value of the water. Slight acidity will cause cohesive tension between the particles, aggregation, and rapid settling. Conversely, slight alkalinity will cause the fine particles to stay in suspension.

High percentages of ferric sulfate, which ionizes with a strong acid value, are present in iron oxide in the process of manufacture until after washing (having previously gone through the processes of grinding and elutriation).

Experimental Procedure

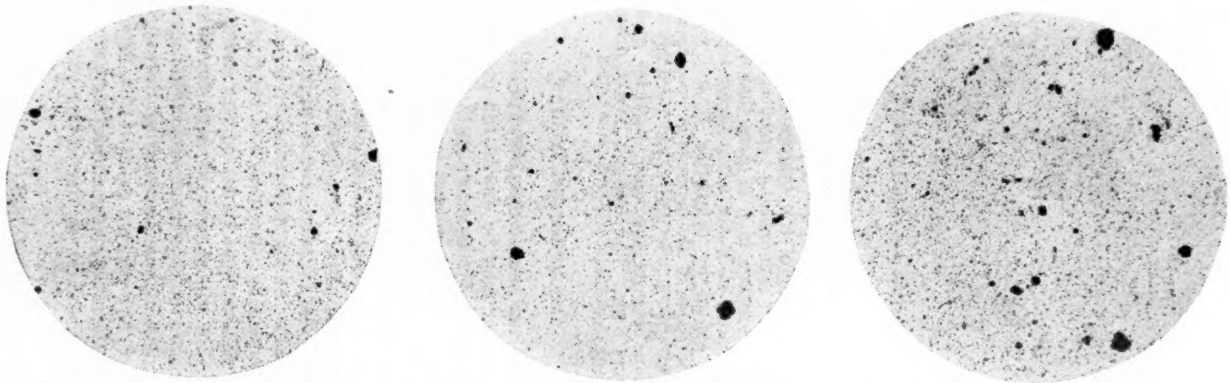
Oxide of iron not thoroughly washed will aggregate in the washing and settling tanks. These aggregates reduce the color value of the pigment and, when incorporated in rubber, will cause poor dispersion and act as nuclei for the formation of larger aggregates.

Five samples of oxide of iron were taken from process. Each sample contained soluble ferric sulfate. Four of the five samples were washed to remove part of the soluble salt. In this manner, samples containing 0.01, 0.05, 1.0, 2.5, and 6.0 per cent ferric sulfate were retained. They were dried and pulverized, and incorporated into the blanc-fixé tube compounds given in Part I. Microsections were taken from each stock by the Allen method (*1*) and examined microscopically. The results of the investigation are shown by the photomicrographs in Figure 1.



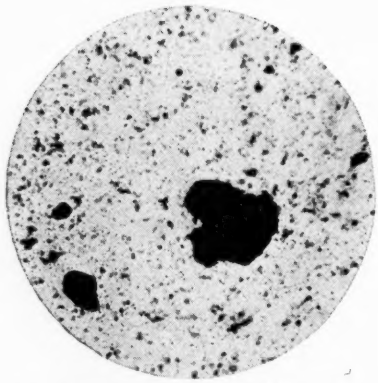
A. 0.01 per cent ferric sulfate (× 100) B. 0.01 per cent ferric sulfate (× 500) C. 0.05 per cent ferric sulfate (× 100)

FIGURE 1. EFFECT OF FERRIC SULFATE ON FORMATION OF AGGREGATES



D. 1.0 per cent ferric sulfate (× 100) E. 2.5 per cent ferric sulfate (× 100) F. 6.0 per cent ferric sulfate (× 100)

FIGURE 1. EFFECT OF FERRIC SULFATE ON FORMATION OF AGGREGATES (*Concluded*)



G. 6.0 per cent ferric sulfate (× 500)

A shows oxide of iron containing 0.01 per cent ferric sulfate. The frequency of aggregates is high, but their relative size is small. B is the same as A at 500 diameters. This gives a clear picture of the character of the aggregates present. C, D, E, and F show the effect of increasing percentages of ferric sulfate. The number of aggregates in F is more than twice as great as in A; the aggregates in F are much larger than those in A. This is clearly shown by comparing B and G. The sharp definition of the edges of the aggregates, particularly those in G, indicate that they act as individual particles and that the cohesive tension between the small particles making up the aggregate is very high. They are not broken down during the milling of the rubber.

Discussion of Results

It is possible that the softening effect of oxide of iron when milling it in rubber may be due to the presence of a large percentage of aggregates as shown in the photomicrographs. These aggregates have sharp and irregular edges which tear apart the globular structure of the rubber.

The color-saturation point of the above oxide is reached at 2 per cent oxide of iron with the standard commercial grade of oxide chosen for this work. Any reduction in the coloring or tinting value of the pigment due to aggregation would be shown by apparent fading of the stock.

If slightly increasing percentages of color are added to a given compound, from 0 to 10 per cent for example, it will be found that a point will be reached at which addition of more color will not improve the overtone and brilliance of the rubber stock. This point is conveniently called the saturation point. It may be at 2, 3, or 8 per cent oxide of iron, depending on the hiding power of the other compounding pigments, on the color of the rubber, or reclaim, or the tinting value of the oxide of iron itself.

The tinting value of a pigment having a particle size greater than the wave length of the corresponding color in the spectrum is proportional to the fineness of the color. Stated in another way, tinting value is proportional to the specific surface of a

unit weight of a pigment. The specific surface of an impalpable pigment is reduced by aggregation of the finer particles—the more aggregates present, the less the specific surface and the lower the tinting value.

Examination of the five stocks, containing increasing amounts of ferric sulfate, for color showed the color to fade in proportion to the amount of ferric sulfate present in the oxide. Sample 5 faded to such an entent that the stock was only a faint pink. The results are shown graphically in Figure 2.

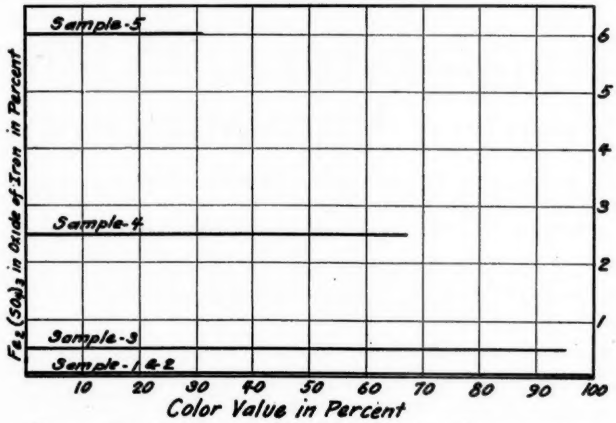


FIGURE 2. EFFECT OF FERRIC SULFATE ON COLOR VALUE

SUMMARY

1. Traces of ferric sulfate in oxide of iron will accelerate aging of rubber.

2. Traces of ferric sulfate in oxide of iron will cut down the rate of cure of rubber.

3. The Bierer-Davis bomb aging tests and the Geer oven tests lead to the same conclusions, although the stocks perform differently in each case.

4. By changing the ferric sulfate to ferrous carbonate with sodium carbonate in solution and washing out the residual sodium sulfate, the ferric sulfate is neutralized to an inactive salt.

5. Iron oxide aggregated by ferric sulfate will not break down on milling in rubber.

6. Increased aggregation reduces the specific surface and the coloring or tinting value of the pigment.

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Temperature Coefficient of Vulcanization

Determination for Mixes Accelerated with Mercaptobenzothiazole and a Crotonaldehyde-Aniline Condensation Product

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THE TEMPERATURE of the inside of a rubber article during vulcanization is much lower than that of the outside because of the low heat conductivity of rubber compounds. Since the curing intensity depends upon the temperature, the cure of the inside of the article is often widely different from that of the outside. In order to evaluate the cure, it is necessary to know accurately how curing intensity varies with temperature. Satisfactory data for mercaptobenzothiazole stocks have been lacking.

The temperature coefficients have been determined for mercaptobenzothiazole mixes and for a mix accelerated by a crotonaldehyde-aniline condensation product. Special care was taken to eliminate errors in temperature regulation, etc., by the use of thermocouples in the samples during cure. The values derived from modulus and combined-sulfur data were found to be 1.91 and 2.30 (av.), respectively, for mercaptobenzothiazole; and 2.32 and 2.67, respectively, for crotonaldehyde-aniline.

DATA accumulated over a considerable period have indicated that, when employing certain accelerators, the temperature coefficient of vulcanization is not the same as when a rubber-sulfur mix is used. The values obtained in the past have been subjected to considerable criticism, and curing results from tires have indicated that the values commonly used for stocks containing mercaptobenzothiazole were too high. The values used have varied for different experimenters between 1.45 and 1.60 per 10° F., or 1.94 to 2.35 per 10° C. In some quarters it seems to have been the practice to use the same temperature coefficient regardless of the type of mix or type of accelerator employed. The present experimental work was conducted with the purpose of determining more accurately the value of the temperature coefficient for mercaptobenzothiazole mixes.

In the procedure of vulcanizing test samples, there are several conditions which introduce errors of some magnitude. Two of these errors were thought to be important enough to warrant the correction of the data:

1. It has frequently been observed that the test sheets do not attain the temperature registered by the press thermometer.
2. When a mold is removed from the vulcanizing press for refilling, it drops considerably in temperature. When it is replaced in the press, some minutes elapse before the mold regains the equilibrium temperature. This mold lag may reduce the effective curing time.

The first of these errors may be reduced to a large extent by proper adjustment of the press temperatures. The second is a difficulty inherent in the curing method. Both may be corrected by following the temperature of the test sample with a thermocouple.

No previous data were available regarding the effect of varying sulfur or accelerator ratios, or the effect of the quantity of pigment used in the mix.

Experimental Procedure

With a view to supplying information on the above points, eight stocks were prepared according to the formulas shown in Table I. It may be seen that these stocks include a number of the common variations to be expected in tire stocks. A large enough batch of each stock was mixed to fill all the curing requirements. Sheets were then cut and stored for use. A two-opening hydraulic press was selected after exploration of the platens with a "thermoboard." This device makes it possible to determine the temperature of a small area of the platen and compare it with the temperature of similar areas over the platen surface. Thermocouples at the surface of the thermoboard were used directly in contact with the platen surface. The check was repeated at each temperature used. The press selected had the smallest temperature variation of any press available (maximum, 1° F. or 0.55° C.).

A range of cures was made at each of a series of temperatures separated from each other by steps at 10° F. (5.56° C.). The sheets were cured in four-cavity steel molds, meeting the recommendations of the Physical Testing Committee of the Rubber Division, American Chemical Society. One mold was placed in each opening of the press, allowing eight sheets to be cured at one time. Before loading the mold, a thermocouple was inserted in each sheet. Each couple was placed in such a way as to be as nearly as possible at equal distances from the flat surfaces of the mold and in the center of the sheet. The time required to load the molds was considerably increased by this procedure, approximately 10 minutes being consumed in inserting the sheets in the mold and placing the mold in the press. This practice was followed in all cures up to and including the 250° F. (121° C.) series. The duplication of temperatures from sheet to sheet was so good that from 260° F. (125° C.) to 310° F. (154.4° C.) only one couple was used in a single sheet placed always in the same stock and in the same mold cavity. This reduced the time of loading of the molds to about 3 minutes and hence reduced the temperature lag due to mold radiation.

Table I. Compositions of Stocks

	Stocks A	B	C	D	E	F	G	H
Pale crepe	100	100	...	100	100	100	100	100
Extracted pale crepe	...	...	100	...	...	...	...	...
Mercaptobenzothiazole	0.3	0.3	0.3	0.2	0.7	0.7	1.0	...
ZnO	5	5	5	5	131	131	5.0	5
Sulfur	3	3	3	6.0	3	3	3	3
Stearic acid	...	4.0	1.5	...	...	4.0	4.0	...
Carbon black	...	...	...	...	...	...	40	...
Crotonaldehyde-aniline condensation	...	...	...	...	...	...	...	1

The effect of the temperature lag of the molds was much smaller than was anticipated. The time required for the sheet to reach temperature equilibrium was 5 to 7 minutes. In order to convert these values to equivalent cure units at the scheduled temperature, a time-intensity curve was drawn for each cure, using a preliminary value of 1.50 for the temperature coefficient of vulcanization. From this curve, with the aid of a planimeter, the equivalent cure was computed. The method used has been outlined in detail by Sheppard and Wiegand (*4*). In spite of the time required to reach temperature equilibrium, the reduction in equivalent cure in no case amounted to more than 3 minutes at the temperature used. In most cases it was less than 1 minute. This amounts to about 1 to 2 per cent of the total equivalent cure at temperatures up to 250° F. (121° C.). At higher temperatures the percentage loss in equivalent cure was higher because of the shorter times of cure. Differences in equivalent cure in a given time between two individual cures at the same temperature never amounted to more than 2 per cent. In practically all cases, at a given temperature the curves relating intensity of curing effect with time were

identical during the period of rise. Mold lag, although taken into consideration in the plotting and calculation of data, affected the results to a very small extent. For example, stock C calculated from the curve as drawn in Figure 4 gives a value of 1.764; stock C calculated from the curve uncorrected for mold lag gives a value of 1.750. The equilibrium temperatures reached by the sheets in the press were in all cases so close to the temperatures scheduled as to produce no measurable effect on the results.

After curing, the sheets were tested, using the Goodyear testing machine. Combined sulfur data were obtained on a sufficient number of sheets to determine the temperature coefficient. The combined sulfur data are given in Table II.

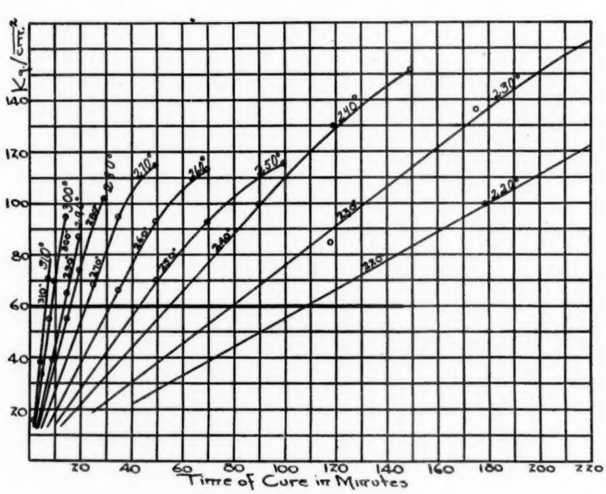

FIGURE 1. STOCK C

TABLE II. COMBINED SULFUR

STOCK	CURE IN MINUTES AT TEMPERATURE SPECIFIED (° C.)[a] 2.3/ 310°	4.6/ 300°	9.1/ 290°	14.25/ 280°	24.25/ 270°	34.25/ 260°	69.7/ 250°	89/ 240°	117.5/ 230°	178.2/ 220°
	%	%	%	%	%	%	%	%	%	%
A	0.38	0.82	0.75	0.74	0.58	0.77	0.55	0.82	0.68	0.72
B	0.24	0.51	0.45	0.52	0.38	0.49	0.55	0.53	0.45	0.48
C	0.45	0.75	0.58	0.71	0.53	0.80	0.83	0.81	0.61	0.70
D	0.52	0.80	0.65	0.74	0.64	0.85	0.85	0.88	0.67	0.38
E	0.41	0.59	0.48	0.74	0.42	0.64	0.62	0.67	0.54	0.58
F	0.28	0.37	0.34	0.96	0.34	0.42	0.36	0.44	0.34	0.68
G	0.41	0.56	0.54	0.52	0.48	0.62	0.81	0.55	0.44	0.34
H	0.82	0.83	0.92	0.89	0.88	0.78	0.74	0.69	0.54	0.50

[a] The cure as given has been corrected for temperature lag of the mold.

Combined sulfur was determined as follows:

A 0.5-gram sample of the stock was extracted overnight in an Underwriter's apparatus. The extracted stock was then transferred to an Underwriter's flask. A mixture of concentrated nitric acid saturated with bromine was added, and digestion carried out at low heat until the bromine fumes were completely expelled. The volume was reduced to 20 cc., and

3 grams of potassium chlorate were added. The solution was then evaporated to dryness. Expulsion of nitric oxide was accomplished by repeatedly evaporating to dryness after addition of hydrochloric acid. The sulfates were then precipitated and ignited in the usual way.

Calculation and Discussion

Modulus may be determined with a greater degree of accuracy then tensile, elongation, or any other commonly used characteristic of the stress-strain curve. For this reason modulus alone was used in calculating the temperature coefficient. In any given case the elongation at which modulus studies were to be made was chosen arbitrarily for convenience

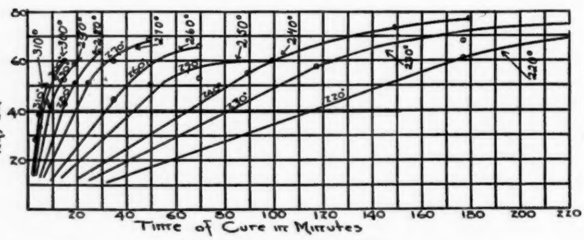

Figure 2. Stock F

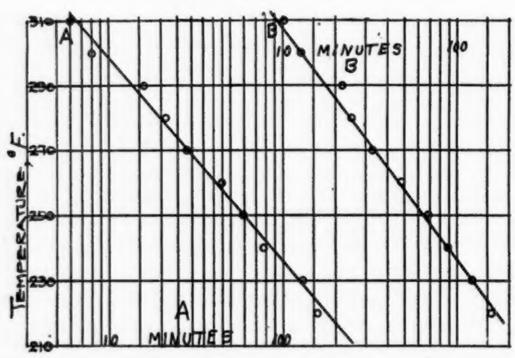

Figure 3. Time of Cure for Standard Physical Properties
Stocks A and B

in plotting. The elongation selected for study of stock C was 800 per cent. Values used for other stocks are shown in the line labeled "Strain" in Table III. The modulus values, read from the stress-strain curves at the chosen elongation, were plotted as modulus-time curves of the type shown in Figures 1 and 2. Figure 1 shows stock C and Figure 2 shows stock F. Similar curves were drawn for each stock. At each temperature the time of cure required to produce a given modulus was read from these curves.

In the case of stock C, for example, the times read were those required to produce a modulus of 60 kg. per sq. cm.

The times of cure so determined were plotted in Figures 3 to 6, against the temperature. The above method is the one in most common use and has been outlined in a previous paper (*1*). A similar procedure was used with the combined sulfur data (Figures 7 to 10).

The temperature coefficients have been calculated (*3*) from these curves and are given in Table III.

TABLE III. TEMPERATURE COEFFICIENTS

	Stocks							
	A	B	C	D	E	F	G	H
			CALCULATED FROM MODULUS DATA					
Strain, %	800	800	800	800	400	400	300	700
Coefficient (10° F.)	1.45	1.38	1.37	1.41	1.45	1.46	1.52	1.60
Coefficient (10° C.)	1.94	1.79	1.76	1.86	1.96	1.97	2.13	2.32
			CALCULATED FROM COMBINED SULFUR					
Coefficient (10° F.)	1.60	1.56	1.55	1.60	1.55	1.57	1.65	1.72
Coefficient (10° C)	2.34	2.28	2.21	2.34	2.21	2.25	2.46	2.67

It is an outstanding fact that the temperature coefficient calculated from physical data is lower than that calculated from combined sulfur data. It is obvious from an inspection of Table II and the individual temperature-coefficient plots, that the combined sulfur data were not as reliable as the physical data. Nevertheless, the differences between the coefficients as calculated from the two sets of data are consistent enough both in direction and magnitude to indicate a definite difference. This being the case, it is evident that a value for the coefficient determined by means of combined sulfur data alone could not be satisfactorily used to predict physical cure. This is in agreement with the fact pointed out by Shepard and Krall (*2*) that degree of physical cure is not related to combined sulfur.

It has been noted frequently that various accelerators seem to have optimum curing temperatures. Figures 1 and 2 indicate that higher modulus values are developed at 220° F. (104.4° C.) to 240° F. (115.5° C.) than at higher temperatures. This behavior seems to be characteristic of stocks accelerated with mercaptobenzothiazole. The data for stock H indicated a much higher optimum. No similar optimum was found for a rubber-sulfur mix (*1*), nor was there any difference between the temperature coefficient derived from physical data and the coefficient calculated from combined sulfur.

The variations in the individual values obtained from the various stocks from A to G may represent an actual difference in behavior. A definite conclusion to this effect should, however, be based upon careful check results. In any case, it seems entirely satisfactory for most practical purposes to use the temperature coefficient obtained by averaging the values given by the seven stocks containing mercaptobenzothiazole. In concluding, it may not be amiss to point out again that, since the present discussion is concerned primarily with physical properties, the value 1.91 per 10° C.

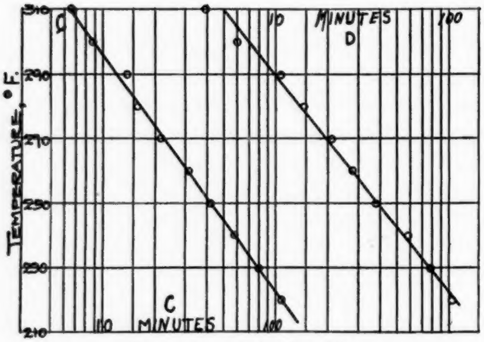

Figure 4. Stocks C and D

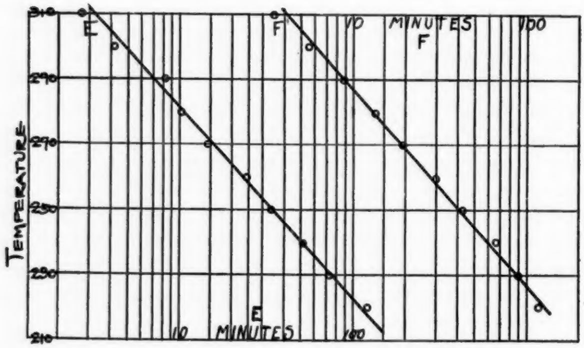

Figure 5. Stocks E and F

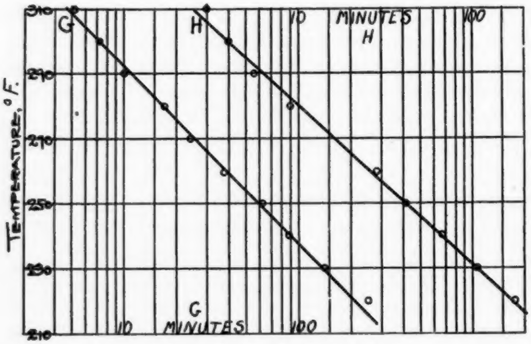

Figure 6. Stocks G and H

TIME OF CURE FOR STANDARD MODULUS

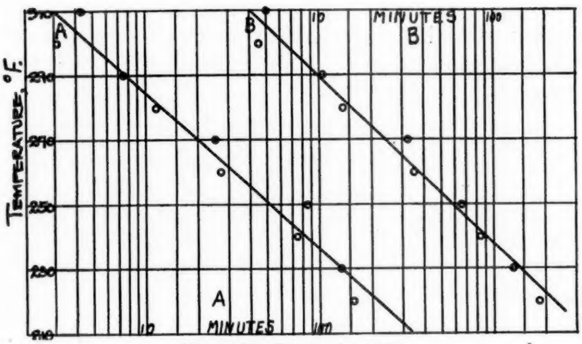

Figure 7. Stocks A and B

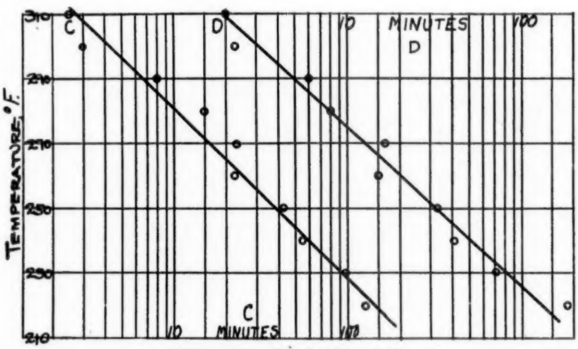

Figure 8. Stocks C and D

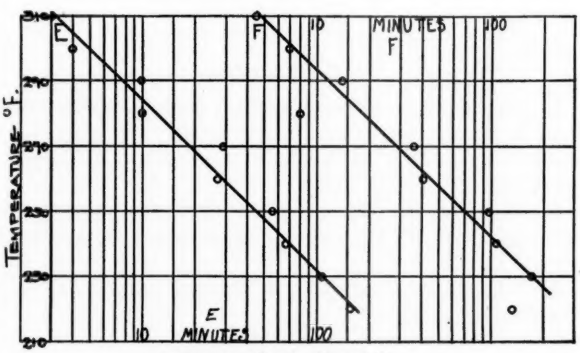

Figure 9. Stocks E and F

Time of Cure for Standard Combined Sulfur

should be used for mercaptobenzothiazole stocks. Likewise, the lower value, 2.32 per 10° C., should be used for the crotonaldehyde-aniline condensation product. The above values have been collected in Table IV, together with the best data available in the literature.

TABLE IV. VALUES OF TEMPERATURE COEFFICIENT

(At 10° C.)

Authority	Rubber Sulfur	Mercapto-benzo-thiazole	Litharge	Croton-aldehyde-Aniline	Alde-hyde-Ammonia
Spence and Young (5)	2.65[a]	..	..	..	..
Van Rossem (7)	2 [a]	..	..	..	..
Twiss and Brazier (6)	2.3[a]	..	..	..	2.4[c]
	2.3[b]	..	..	..	..
	2.4[b]	..	..	..	..
	2.6[c]	..	..	..	..
Park (1)	2.50[b]	..	..	..	..
	2.50[a]	..	..	..	..
Park and Maxwell	..	1.91[b]	..	2.32[b]	..
	..	2.30[a]	..	2.67[a]	..
Sheppard (3)	..	..	2.59[c]	..	..

[a] Combined sulfur. [b] Physical data. [c] Average value.

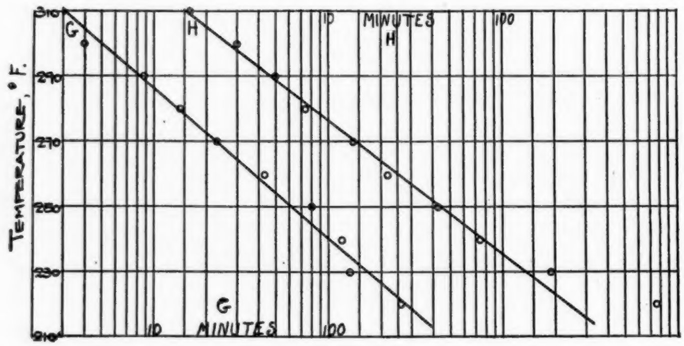

Figure 10. Stocks G and H

TIME OF CURE FOR STANDARD COMBINED SULFUR

CONCLUSIONS

1. The average temperature coefficient of mercaptobenzothiazole accelerated mixes, based upon physical data, was found to be 1.91 per 10° C. For crotonaldehyde-aniline, the value was 2.32 per 10° C.

2. Based upon combined sulfur data, the value was 2.30 (average) per 10° C., and for crotonaldehyde-aniline 2.67 per 10° C.

3. The values obtained from physical data are to be preferred for all practical purposes.

ACKNOWLEDGMENT

The authors are indebted to H. W. Wilson for assistance in the experimental work, and to R. P. Dinsmore for kind permission to publish the results.

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Measurement of Average Particle Size of Fine Pigments

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A method of obtaining excellently dispersed suspensions of rubber pigments of accurate concentration is described in which the pigment is milled into rubber and the stock then dissolved in a solvent.

The average particle sizes of carbon blacks measured by the Zsigmondy count method were found to range from 0.061μ for rubber gas black to 2.22μ for the coarsest one measured. The zinc oxide pigments had average particle sizes from 0.076μ to 0.57μ. Measurements on several other pigments of interest are included. Because of the high visibility in the ultra-microscope, this method gives smaller values for average particle size than the photomicrographic methods.

The results have been used to calibrate a microturbidimeter of the extinction type for use in measuring average particle size.

Curves are included showing how the turbidities of suspensions of zinc oxide and carbon black vary with the average particle size, concentration, and wave length of light used.

THE reënforcing properties of pigments used in rubber compounding and the milling characteristics of these pigments are so intimately connected with their degree

of fineness that considerable interest is attached to securing measurements of their average particle size. Much work has been done on the measurement of the particle size of microscopic and ultra-microscopic material, and a number of methods have been devised which, when properly used, yield satisfactory results. Svedberg (*24*) gives an excellent discussion of these methods. Similarly, Green (*11*) gives a very complete discussion of the theory of average particle size and the significance of average diameters, and Wells (*27*) a résumé of the field of turbidity measurements.

The particle size of rubber pigments ranges from the definitely microscopic well into the colloidal region. Two of the most important are carbon black and zinc oxide, and it is these pigments which have been investigated most thoroughly, although a few others of interest have been studied.

Considerable work has been done on the determination of the particle size of carbon black, but the literature contains varying figures. The value given by Spear (*21*), 0.1–0.2μ up to about 0.6μ, has been widely quoted. Green (*9*) gives the size of gas black as about 0.15μ. Peterfi, for A. Wegelin (*26*), determined by the Zsigmondy count method the average particle size of three German carbon blacks as 0.124, 0.106, and 0.083μ. More recently (for F. Hartner, *13*) he gives 0.050μ for the average diameter of gas black. J. J. Barnard, in a communication to Wiegand (*28*), reports by ultra-filtration and counting in ultra-violet light an estimated average particle size of gas black as 0.05–0.06μ. Grenquist (*12*) estimated gas black as ranging from 0 015 to 0.200μ.

Parkinson (*17*) makes no estimate of the particle size of gas black, but quotes the particle size of lampblack as about 0.3–0.6μ, which agrees well with Green's estimate, 0.3–0.4μ. Moore (*15*) gives for the particle size of Thermatomic black, 1.0μ, and for P-33, 0.23μ.

Most of the results which have been published on the average particle size of zinc oxide pigments have been obtained by Green's (*11*) photomicrographic method or modifications thereof. In the papers of Green (*10, 11*), Haslam and Hall (*14*), and Stutz and Pfund (*23*) can be found a large number of measurements for every type of zinc oxide. The values quoted in Table III, supplied by the New Jersey Zinc Co., were obtained by the method of Stutz and Pfund (*23*).

It is the purpose of this paper to set forth an accurate and efficient method for measuring particle size. Since the authors are directly concerned with the particle size of rubber pigments as dispersed in rubber, and not as dispersed in an aqueous medium or rubbed out on a slide, the turbidity of xylene-rubber-pigment cements prepared by milling the pigment into the rubber and swelling in xylene has been used as the basis of this method. The turbidimeter used in this work was the microturbidimeter used previously by Gehman and Ward (*7*).

Since the turbidity of suspensions is affected by a number of variables not readily calculable, a turbidimeter to be used for particle-size measurements must be calibrated with pigments whose particle size has been determined by an independent method. For calibration of the turbidimeter the count method with the cardioid ultra-microscope of Siedentopf (*18*), manufactured by Zeiss, has been used.

Average particle sizes as determined by the count method together with turbidimetric measurements have been obtained on a series of carbon blacks, a series of zinc oxides, and a few other pigments of interest in the rubber industry. The carbon blacks used varied in particle size from 0.025 to 2.22μ, and the zinc oxides from 0.076 to 0.566μ.

Theory of Microturbidimeter

The microturbidimeter is an extinction type of turbidimeter. When the light from the filament enters a suspension of a white pigment, it undergoes a loss of intensity because

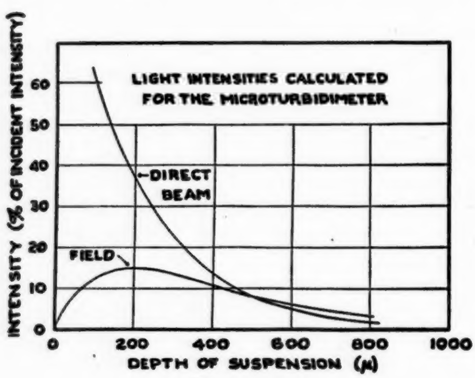

Figure 1

of light scattering by the disperse phase. The process of extinction consists in having the diffuse field due to the scattered light of the same intensity as the direct beam. The way in which the scattered intensity and direct intensity vary to produce this result is explained as follows:

Let I_0 = intensity of incident beam before any scattering
I_x = intensity of incident beam after penetrating a depth x
I_s = intensity of forward scattered light at x

Also let dI_s be the light scattered in the forward direction from an element of depth dx which we think of as having unit cross section. The intensity dI_s will be diminished exponentially as it proceeds in the direction of x, according to Lambert-Beer's well-known law (*25*).

The intensity of the direct beam at x will be, in accordance with the same law

$$I_x = I_0 e^{-kx} \tag{1}$$

k is a constant for any one suspension, concentration, and wave length. The increment of scattered light, dI_s, will be proportional to I_0e^{-kx} and to dx. Hence

$$dI_s = AI_0e^{-kx}\,dx \qquad (2)$$

A is a constant.

By the time dI_s penetrates to a depth d, its intensity will be $dI_se^{-k(d-x)}$, assuming monochromatic light. This will be its contribution to the intensity of the scattered light at d.

The total intensity of the scattered light will be the integral of all the contributions from the small elements between $x = 0$ and $x = d$, hence

$$I_s = \int_0^d e^{-k(d-x)}dI_s$$

From Equation 2

$$I_s = \int_0^d e^{-k(d-x)}AI_0\,e^{-kx}dx$$

$$I_s = \int_0^d AI_0\,e^{-kd}dx$$

$$I_s = AI_0\,de^{-kd} \qquad (3)$$

To a first approximation this is the intensity of the forward scattered light at depth d.

When the intensity of the direct beam equals the intensity of the scattered light—i. e., at the extinction depth d_e—we have

$$I_x = I_s$$

$$I_0e^{-kd_e} = AI_0d_ee^{-kd_e}$$

$$A = \frac{1}{d_e}$$

So A is the reciprocal of the extinction depth.

Introducing this value of A in Equation 3, we get the intensity of the forward scattered light at depth d to be

$$I_s = I_0\frac{d}{d_e}\,e^{-kd} \qquad (4)$$

I_s has a maximum for a value of d which can be obtained by differentiating Equation 4 and equating to zero. The result which comes out of this procedure is that the scattered light has its maximum intensity for a value of d equal to $1/k$.

Figure 1 is a plot of Equations 1 and 4 for arbitrarily assumed values of k and d_e, and helps to visualize how the intensity of the scattered light and of the direct beam vary so as to achieve equality at one point—i. e., where the curves intersect. k was taken equal to 0.005 and d_e to 500μ in order to plot the curves.

Equations 4 and 1 express the fact that the extinction depth is independent of the filament intensity. This is the case for white pigments and for latex. Since it is not strictly

true for carbon black suspensions (see Figure 5), the equations would have to be modified for the cases where light absorption is important.

Calculation of Particle Size from Adhesion-Tension Measurements

Superspectra gas black is so fine that the ultra-microscope was not suitable for its measurement, as the results obtained indicated that it was but slightly smaller than Micronex, whereas other properties indicated that it was much smaller. An estimate of the average particle size for a series of blacks, one of which is similar to Superspectra, can be made from data which have been published by Bartell and Smith (*3*) on the pore radii of carbon black diaphragms used in adhesion-tension measurements. The method used in making this estimate is as follows:

Let n = number of particles per unit volume
R = radius of pores
x = number of pores per unit surface
r = radius of particle
d = diameter of particle
v = volume in unit volume unoccupied by particles

The work of Smith, Foote, and Busang (*20*) on the packing of spherical lead shot under various conditions showed that a mean exists between cubic and hexagonal packing depending upon the method of packing, high-pressure packing approaching the hexagonal. They have worked out v for cubic packing as 0.4764, and for hexagonal packing 0.2595. For both types of packing, since there will be $\sqrt[3]{n}$ particles along an edge of a unit cube, $x = n^{2/3}$.

Using these facts, we have for the two types of packing the following equations:

Cubic Packing

$$n = \frac{1}{8r^3}$$
$$x = \frac{1}{4r^2}$$
$$v = \pi R^2 x$$
$$v = \frac{1}{4r^2}\pi R^2$$
$$0.4764 = \frac{\pi R^2}{4r^2}$$
$$d = 2.568R$$

Hexagonal Packing

$$n = \frac{\sqrt{2}}{8r^3}$$
$$x = \frac{\sqrt[3]{2}}{4r^2}$$
$$v = \pi R^2 x$$
$$v = \frac{\sqrt[3]{2}}{4r^2}\pi R^2$$
$$0.2595 = \frac{\sqrt[3]{2}}{4r^2}\pi R^2$$
$$d = 3.907\,R$$

Table I gives the values of pore radii reported in a paper by Bartell and Smith (*3*) on the adhesion tension of a series of blacks, together with the values computed from them of the particle diameters on the assumption of hexagonal packing and on the assumption of cubic packing. It is interesting to note that the value for rubber gas black is of the same order as that secured by the ultra-microscopic

count method. On the assumption that Superspectra was about the same as the specimen designated "color gas black," the value of 0.025μ has been introduced into Table II as being the best estimate available for the particle size of this black.

TABLE I. PARTICLE SIZE FROM PORE RADII MEASUREMENTS

Sample	Source	Pore Radius	Limits of Particle Size: Hexagonal packing	Cubic packing
		μ	μ	μ
A	Lampblack	0.0793	0.316	0.204
B	Thermal decomposition	0.0780	0.305	0.200
C	Thermal decomposition	0.0226	0.089	0.058
D	Rubber gas black	0.0173	0.068	0.045
E	Ink gas black	0.0190	0.075	0.049
F	Ink gas black	0.0183	0.072	0.047
G	Color gas black	0.0076	0.030	0.020

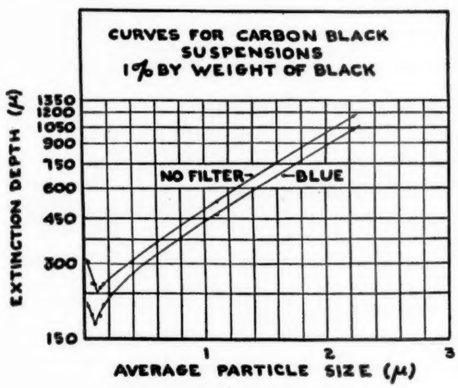

FIGURE 2

PREPARATION OF SUSPENSIONS

Aqueous suspensions of carbon black containing saponin and gum arabic as protective colloids milled in a small ball mill proved unreliable, since the turbidimeter readings depended on the time of milling and the amount of protective colloid. On the other hand, it was found that carbon black dispersed in rubber, remilled several times, and then made into a xylene cement, was completely deflocculated, and that readings could be duplicated closely. This technic was therefore adopted for all the pigments studied in the preparation of the suspensions for the turbidimeter. The carbon blacks were selected to cover the entire range from the coarsest to the finest. The carbon black was incorporated on an 18-inch laboratory mill.

The rubber was broken down on a warm mill. The carbon black was added until the batch came exactly to the desired weight. It was then cooled, remilled, cooled, and milled with an equal weight of clean pale crepe sheet. This batch was remilled until the dispersion was shown to be complete by microscopic examination using the squeeze-

out method (*1*). In the case of Superspectra it was found necessary to dilute the stock further in order to get a smooth cement free from aggregates.

Xylene cements were then made up of the entire series of stocks, 1 per cent carbon black, 4 per cent rubber by weight, or 0.482 per cent carbon black by volume. The weighing was done on an analytical balance. Cements of different concentrations were prepared similarly. The cements were allowed to stand with occasional shaking until the dispersion appeared to be complete by microscopic examination.

The dispersions of zinc oxide were prepared in essentially the same manner by milling equal weights of zinc oxide and pale crepe rubber until microscopic examination by the squeeze-out method showed the dispersions to be satisfactory. Cements were then prepared of the desired concentrations by dissolving weighed amounts of stock in weighed quantities of xylene. All of the cements were examined microscopically to be sure the dispersions were complete.

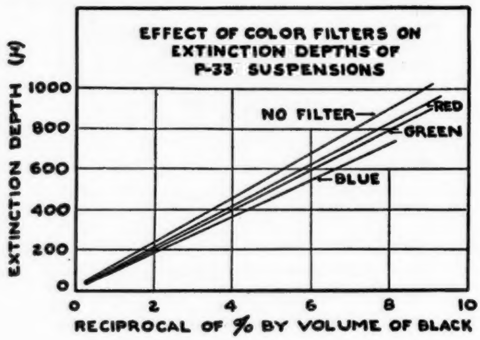

FIGURE 3

To secure very concentrated suspensions, evaporation of the more dilute cements was resorted to. A few cements in carbon disulfide and gasoline were prepared in the same manner as in xylene, the concentrations being calculated on a volume per cent basis to make them comparable with the xylene cements.

COUNTING PROCEDURE

With the invention of the slit ultra-microscope by Siedentopf and Zsigmondy (*19*), measurement of the particle size of colloids was first made possible. In the slit ultra-microscope the light enters the colloidal suspension at right angles to the axis of the microscope, the presence of the colloidal particle being indicated by a point of light on a dark background. Subsequent improvements such as the cardioid ultra-microscope of Siedentopf (*18*), the system used in the present investigation, have increased the usefulness of the instrument by increasing the resolving power of the system. The cardioid ultra-microscope differs from the slit ultra-

microscope in that the illuminating pencil and diffracting pencil of rays which go to form the image are coaxial; the rays of greater aperture are employed to illuminate the object while those of smaller aperture are made to reach the eye, resulting in a brighter image.

The Zeiss cardioid ultra-microscope consists of a cardioid dark-ground condenser, a fused quartz counting chamber with holder, a 3-mm. glycerol immersion objective having a maximum N.A. of 1.0 with an iris aperture stop, and a 30X positive eyepiece all readily adapted to any microscope equipped with a substage rack. A clock-feed carbon arc with a water-cell heat filter was used for the illuminating system.

For estimation of the particle size a restricted volume of known dimensions is necessary. This was obtained by inserting in the ocular an Ehrlich stop giving a field 0.0163 mm. square. The depth of the cell was measured by focusing and was found to be 5.0μ.

In using the cardioid ultra-microscope, one of the prime

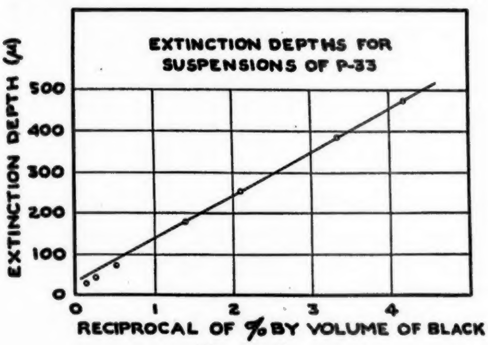

FIGURE 4

essentials is that the cell be absolutely clean. It was cleaned by boiling in cleaning solution, washing in hot distilled water, drying over a hot plate, and heating for a short time in a Bunsen flame. The system was aligned by an eccentric objective centering mount and the illumination centered by reflecting the image of the crater back into the arc. A drop of the suspension was placed in the cell which was clamped in the holder. The condenser was connected to the cell with a drop of water, the objective to the cell with a drop of glycerol, and the system adjusted until the images appeared as brightly illuminated, sharply defined spots against a dark background.

The suspensions for counting were prepared by dispersing one or two drops of the xylene cement in an appropriate weight of Nujol, the amounts being carefully weighed on an analytical balance. After standing a day or so with occasional shaking, complete dispersion was obtained. These cements are highly useful for counting, since Nujol itself

is optically empty and the Brownian motion of the particle is almost completely stopped. Since rubber itself is not optically empty, a blank rubber cement was dispersed in Nujol at a somewhat higher concentration than that used for counting, the count averaging less than one particle per field, owing to the high dilution. The concentrations of the Nujol cements for counting were adjusted so as to yield as near 20 particles per field as possible. Usually twenty fields were counted and the averages obtained were duplicable.

Sample Calculation with Micronex Gas Black

Wt. of xylene cement, 1% black by wt., gram	0.0229
Wt. of Nujol, grams	49.1335
Density of Nujol at 25° C.	0.8848
Density of black	1.80
Av. of 20 fields, particles per field	25

$$D = \frac{1}{0.0001}\sqrt[3]{\frac{6\,CV}{\pi\rho n}}$$

Where D = average diameter in μ
C = concentration of pigment, grams per cc.
V = volume of field counted
ρ = density of pigment
n = average count

$$D = \frac{1}{0.0001}\sqrt[3]{\frac{6\,\dfrac{(0.0229)(0.01)(0.8848)}{(49.1335)}(0.00163)^2(0.0005)}{(3.1416)(1.8)(25)}}$$

$$D = 0.061\mu$$

Discussion of Microscopical Methods

Results obtained by the count method would be expected to be smaller than those given by the photomicrographic method for the following reasons:

In the ultra-microscope, particles as small as 0.010 to 0.015μ can be rendered visible since the perception of the particles depends rather on the following factors (*24*) than on the resolving power: (1) specific intensity of light source, (2) aperture of illuminating system, (3) contrast in the field of view, and (4) light-emitting power of particles.

In photomicrographic methods, on the other hand, the numerical aperture of the objective limits the size of the smallest particles resolved to about 0.2μ for visible light and 0.1μ for ultra-violet light.

In the ultra-microscopic count method for the determination of particle size, the depth of the counting chamber is always a source of possible error. Since it is only a few microns in depth, it taxes to the limit most methods of micrometry. Several methods for measuring the cell depth have been tried, including the use of an adaptation of the optical lever of Bond (*4*). By this device a value of 2.0μ ± 0.2μ was obtained for the difference in height between the center and edge of the cell chamber. But when the cell was assembled focusing on the upper and lower surfaces of the chamber with the microscope fine adjustment gave an

average value of 5.0μ, which is somewhat higher than the average value of all methods used and may be considered as a maximum. This value has been used for all calculations.

When the cell is filled with the Nujol counting cement, no correction for refractive index is necessary since the system is virtually homogeneous. A fortunate aspect of the situation is that in calculating the average diameter the depth of the cell enters into the formula as the cube root. It may be stated that the probable limit of accuracy of the method is ± 10 per cent, owing to errors in counting and measurements of the counting volume.

Although the photomicrographic method may be an excellent and useful one for coarse pigments, the authors believe that the finer pigments are actually much smaller than this method would indicate, for three reasons:

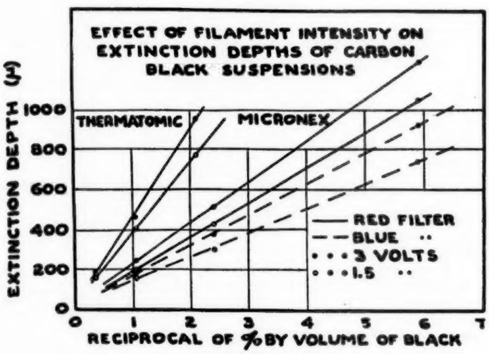

FIGURE 5

1. Particles of the finer pigments are near the limit of resolution for visible light, and the full theoretical resolving power of a system is rarely realized. A pigment whose average particle size is at the limit of resolution will have a large number of particles which are too small for resolution. Particles below the limit of resolution will appear enlarged (*2*).
2. It is impossible to get all the particles in the same focal plane, and since objectives of high N. A. have a very slight focal depth, enlarged images and circles of confusion will result.
3. No present method of preparing slides will yield as complete a dispersion as can be obtained by other means, such as milling the pigment into rubber.

For pigments for which direct illumination is suitable, the method of Dunn (*6*), in which the image is projected on a screen and thereby permits one to focus the particle being measured, seems preferable to the regular photomicrographic procedure.

RESULTS

In Tables II, III, and IV are given the average particle sizes, obtained by the count method, of the pigments used in calibrating the turbidimeter. Superspectra, listed in Table II, is a special gas black known as a color black, and Micronex

is a regular rubber gas black. P-33, Thermatomic, and Velvetex are all thermal-decomposition blacks supplied to the rubber trade, and are known as soft blacks.

TABLE II. PARTICLE SIZE OF CARBON BLACK PIGMENTS OBTAINED BY COUNT METHOD

PIGMENT	AV. PARTICLE SIZE
	μ
Superspectra[a]	0.025
Micronex	0.061
Special sample (rubber gas black)	0.092
Shewinnegan acetylene black	0.130
P-33	0.159
Thermatomic[b]	1.12
Velvetex[b]	2.22

[a] Estimated.
[b] Counted in blood count cell

TABLE III. PARTICLE SIZE OF ZINC OXIDE PIGMENTS OBTAINED BY COUNT METHOD

PIGMENT	AVERAGE PARTICLE SIZE	
	N. J. Zinc Co. values	Count method
	μ	μ
1	0.11	0.076
2	0.15	0.099
3	0.28	0.159
4	0.32	0.185
5	0.70	0.566

TABLE IV. PARTICLE SIZE OF MISCELLANEOUS RUBBER PIGMENTS OBTAINED BY COUNT METHOD

PIGMENT	PARTICLE SIZE
	μ
Red iron oxide	0.139
Titanium oxide	0.190
Blanc fixe	0.245
Special blanc fixe	0.160

All of the zinc oxides, together with the values for the particle size as obtained by the method of Stutz and Pfund (*23*), have been supplied by the New Jersey Zinc Co. The pigments appearing in Table IV are regular commercial grades.

DISCUSSION OF TURBIDIMETER MEASUREMENTS

The microturbidimeter used in this work has previously been described in detail (*5, 7*). It operates on the extinction principle. An incandescent filament is viewed through a film of the suspension contained between a convex lens and a flat glass plate. The turbidity of the suspension is measured by the depth of it required to produce extinction of the filament, or rather, by the reciprocal of this depth.

The radius of curvature of the lens used in the extinction cell of the turbidimeter was 8.636 cm. Red, green, and blue color filters were used. The red filter was a Wratten filter. The green was a Corning filter known as Sextant Green. For a blue filter, a combination of Corning light theater blue and dark heat-resisting blue was used. Unless the green and blue filters used with the microturbidimeter are very free from red transmission, as is difficult to judge from transmission curves obtained photographically, the filament shows

a reddish tinge just prior to extinction which vitiates the comparisons.

Figure 2 gives the calibration curve for the measurement of the average particle size of carbon blacks with the microturbidimeter. The minimum extinction depth occurs for an average particle size of about 0.11μ, but this depends somewhat on the wave length of light used. It shifts toward a smaller value of the particle size for shorter wave lengths. The same phenomenon has been observed by Stutz (*22*) for suspensions of zinc oxide.

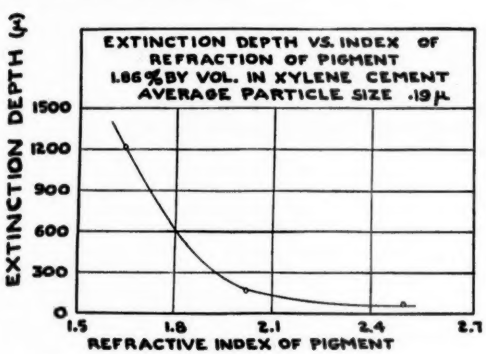

FIGURE 6

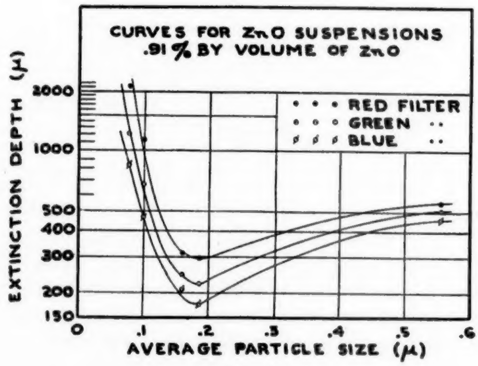

FIGURE 7

The curves in Figure 2 show that the count method of determining average particle size yields results which correlate well with the turbidity measurements in the sense that they are smooth curves. However, anomalous turbidimeter readings can be obtained by mixing blacks of widely different average particle size, so that the fact that smooth curves were obtained indicates that, in general, the carbon blacks had similar size-distribution curves.

Figure 3 shows the straight-line relation existing between the reciprocal of the concentration and the extinction depth

for suspensions of P-33, with the different light filters used. In Figure 4, the line is extended to higher concentrations, the most concentrated cement used being 7.91 per cent by volume of black and having an extinction depth of only 28μ. The points in Figure 4 show a slight systematic deviation from a straight line, the curve bending toward the origin. For zinc oxide (see Figure 8), the linear relation holds all the way down to an extinction depth of about 30μ, corresponding to a concentration of 12.4 per cent by volume of zinc oxide. This was as high a concentration as could conveniently be obtained. It is interesting to compare these results with those previously reported for latex (*7*).

The dependence of turbidity on concentration for high concentrations and the appearance of a maximum such as occurs for latex is not well understood, although such maxima have been reported for other systems (*16*, *25*).

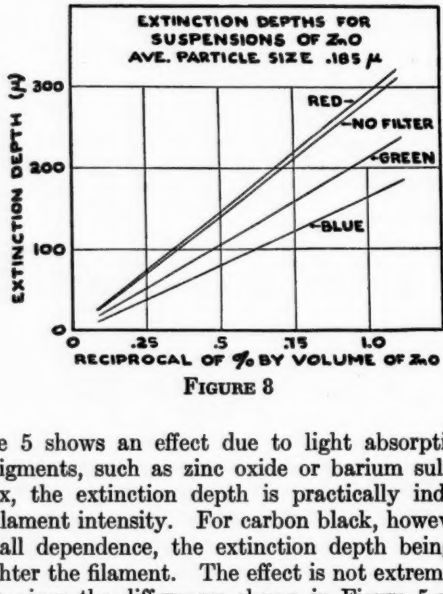

FIGURE 8

Figure 5 shows an effect due to light absorption. For white pigments, such as zinc oxide or barium sulfate, and for latex, the extinction depth is practically independent of the filament intensity. For carbon black, however, there is a small dependence, the extinction depth being greater the brighter the filament. The effect is not extremely large, however, since the differences shown in Figure 5 were produced by a twelve-fold change in filament intensity. Measurements with color filters, for carbon black, have not taken account of differences in intensity of the transmitted light. This may explain why carbon black suspensions show better transmission with no filter than they do with a red filter, whereas the reverse is the case for zinc oxide (see Figures 3 and 8).

The turbidity of a suspension is dependent among other things on the difference in the index of refraction of the two phases, so that in general a change in the index of refraction of the medium can be used to secure information about the index of refraction of the dispersed phase. It

was thought that it would be interesting to do this for an absorbing dispersed phase such as carbon black.

For this purpose, additional suspensions of carbon black in carbon disulfide and in gasoline cements were prepared. For this range of the index of refraction, 1.489 to 1.617, the extinction depth showed no significant variation.

Figure 6 shows the effect of the index of refraction of the pigment on the extinction depth, giving the curve obtained by plotting the extinction depths for suspensions in xylene cement of barium sulfate, zinc oxide, and titanium oxide against their refractive indices which are respectively 1.64, 2.02, and 2.50.

In Figure 7 we have the calibration curves for the turbidimeter which make possible its use for measuring the average size of zinc oxide pigments. If there is any question as to which side of the minimum the pigment belongs, it can usually be answered by taking readings with the red and with the blue filters. The ratio of these two readings is different on the two sides of the minimum.

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The Determination of Sulfur in Rubber by Means of the Calorimetric Bomb

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For determining the total sulfur content of rubber, industrial laboratories ordinarily use some method which is based on the destruction of the organic substances, and oxidation of the sulfur to sulfur dioxide in an open vessel, *e. g.*, by sodium peroxide, perchloric acid, or a potassium carbonate-potassium nitrate mixture.

Particular attention should be called to the method of Butironi[1] which is based on the fusion of the substance with dry potassium hydroxide in a silver crucible, and subsequent oxidation of the sulfur to sulfuric acid by potassium nitrate. This method can be used for hard rubber.

There is also an interesting method of Losana,[2] which involves heating the substance with powdered iron and sodium bicarbonate, treatment of the iron sulfide with hydrochloric acid, passage of the hydrogen sulfide into zinc acetate solution, addition of a known excess of iodine solution, and titration of the excess iodine.

All these methods are tedious and delicate, and leave much to be desired from the point of view of precision because of losses through spattering or incomplete oxidation.

Because of this, and because of the great simplicity and rapidity of execution with many organic substances other than rubber, the possibility of utilizing the calorimetric bomb for the determination of sulfur in rubber was investigated.[3,4] Many tests on mineral oils and organic substances containing sulfur have proved the simplicity of the method and the certainty of perfect combustion and complete oxidation of the sulfur when the procedure is carried out with proper skill.

In determining total sulfur in rubber, the method found so well suited for mineral oils and other sulfurated organic substances was used without modification. The instantaneous combustion was carried out in a Kroecker calorimeter bomb in the presence of oxygen under a pressure of 30 atmospheres. To the sample in the crucible was added a small quantity of a liquid of high calorific power (decalin with 10,868 calories) with the object of obtaining complete combustion. In the bottom of the bomb was placed a certain quantity of distilled water to assure complete condensation of the sulfur dioxide formed.

The method is very simple. Weigh 0.1–0.3 gram of finely divided rubber directly in a platinum or a quartz crucible in the calorimetric bomb, add about 1 cc. of decalin, immerse an iron spiral in the liquid for the purpose of ignition, and after putting 10 cc. of distilled water in the bottom of the bomb, close the latter, fill it with oxygen to 30 atmospheres' pressure, and close the electric current.

After the combustion is over, cool the bomb, allow the gas to escape slowly, and open the bomb after twenty to thirty minutes. It is not necessary to pass the gas into a solution of sodium carbonate to catch any sulfurous gas nor to oxidize it with bromine water and to add this liquid to the main solution, because oxidation is always complete. After the bomb is opened, wash it carefully with hot water, together with the crucible, and collect the wash waters in a 300–350 cc. beaker.

Precipitate with ammonia the traces of iron present (the iron spiral and lining of the bomb are of special steel), filter, acidify with hydrochloric acid, and determine the sulfur gravimetrically as barium sulfate. The extremely satisfactory results obtained by this procedure in comparison with those by the peroxide method—even when the latter is carried out with the greatest care and in duplicate—for different types of technical rubber mixtures are shown in the following table.

Expt. No.	Type of Rubber	Quantity Analyzed in G.	$BaSO_4$ Found in G.	% Sulfur Peroxide Method	% Sulfur Calorimetric Bomb
1	Red Michelin	0.6550	0.0710	1.48	..
		0.1260	0.0140	..	1.59
2	Black Michelin	0.5000	0.1760	4.83	..
		0.1010	0.0374	..	6.08
3	Pirelli	1.0000	0.3650	5.01	..
		0.1922	0.0786	..	5.62
4	German No. 1, not vulcanized	0.5500	0.0803	2.00	..
		0.1544	0.0235	..	2.09
5	The same, vulcanized	....	....	2.00	..
		0.1210	0.0183	..	2.07
6	German No. 2, not vulcanized	1.0008	0.2200	3.05	..
		0.1346	0.0310	..	3.16
7	The same, vulcanized	....	....	3.01	..
		0.1432	0.0322	..	3.07
8	German No. 3, not vulcanized	0.9054	0.3239	4.76	..
		0.1610	0.0568	..	4.82
9	The same, vulcanized	....	....	4.76	..
		0.1004	0.0350	..	4.80

As can be seen, these results leave nothing to be desired. The peroxide method gives somewhat lower values, as is generally recognized. A control experiment with the Carius method was not considered necessary, since the precision of the bomb method has been confirmed in the earlier works referred to, where chemically pure substances containing sulfur were burned.

In addition to the greater precision of the calorimetric method, the extreme simplicity and rapidity with which the results can be obtained make its adoption advisable in the field of rubber. In little more than half an hour it is possible to reach the stage of the barium sulfate, in contrast to several hours required by the other method.[5]

There is no appreciable consumption of reagents, and tests need not be made in duplicate and blank, because combustion of the rubber is always complete, whereas with the other methods there is at times a carbonaceous and spongy residue of incompletely burned products. It has been observed, however, and the fact is of the utmost importance, that in order to avoid the same inconvenience in the bomb crucible, it is necessary to limit the quantity of rubber to be burned to that requisite for the gravimetric determination of the sulfur. Moreover, an excessive quantity of decalin must not be used, for otherwise the temperature of combustion will be raised too high, with consequent deleterious effect on the life of the apparatus, and contamination of the reaction product with an appreciable quantity of carbon. Tests carried out under these conditions, *e. g.*, with 0.500 gram of rubber and more than 1 cc. of decalin, have given bad results, because of imperfect combustion, as shown by the presence in the crucible of a swollen mass of carbon black. On the other hand, by limiting the quantities of the same type of rubber and liquid hydrocarbon, this inconvenience is immediately overcome.

An objection might be raised to the high cost of the calorimetric bomb. This

was, however, more true in the past than at the present time. In Italy excellent apparatus is made at reasonable prices so that the calorimetric bomb is no longer a prerogative of the scientific laboratory, but is now a practicable adjunct in every industrial field. In the determination of sulfur, neither the calorimetric bath nor a thermometer divided into hundredths of a degree is necessary. The only cost is the simple bomb, which today is best constructed of special steels of the V2A type which are not attacked by chemical reagents, and which fitted with accessories —attachments, electric resistance, tubes and a manometer for the oxygen—can be obtained at a cost which is not excessive, as was the old platinum apparatus, but at a cost of less than a thousand lire.

In conclusion it should be mentioned that, if one-half hour at the most is consumed for each bomb determination, it is possible by weighing the next substance in the interval to carry out a large number of determinations in the same day, as is ordinarily required in control work.

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[5] When antimony sulfide is present in the rubber mixture, the determination of sulfur is more complicated, as with other methods. In the case of barium sulfate, it is sufficient to separate it as an insoluble residue after combustion in the bomb and before precipitation with barium chloride of the sulfur trioxide formed. This problem is to be considered in detail in a later paper.